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Thermodynamic Study of Small Silicon Carbide Clusters with a Mass Spectrometer

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The Knudsen effusion mass spectrometric method has been used to measure the equilibrium partial pressures of SiC_2, Si_2C, Si_2C_2, and Si_3C above the SiC−graphite system at temperatures between 1750 and 2000 K. New thermal functions have been calculated for these molecules from recent literature experimental and theoretical molecular parameters and combined with the measured partial pressures to obtain the atomization enthalpies, $\Delta H_{a,0}$, in kJ mol^{-1}: 1247 ± 8 (SiC_2), 1052 ± 10 (Si_2C), 1652 ± 14 (Si_2C_2), and 1437 ± 14 (Si_3C). The derived enthalpies of formation, $\Delta H_{f,298}$, in kJ mol^{-1}, are 633 ± 9 (SiC_2), 566 ± 11 (Si_2C), 678 ± 15 (Si_2C_2), and 632 ± 15 (Si_3C).

Introduction

A good understanding of the vaporization behavior of SiC at high temperatures may lead to new insights into the low-pressure chemical vapor deposition of SiC,[1] the use of SiC as a support material for high-temperature catalysts,[2] the development of new high-temperature structural materials,[3] and high-temperature semiconductors.[4] The thermodynamics of small silicon carbide clusters can aid our understanding of stellar dynamics.[5] The bonding in small silicon carbide clusters is of chemical interest since carbon readily forms double bonds with itself whereas silicon generally does not form double bonds.[6]

Drowart et al.[7] were the first to use the Knudsen effusion mass spectrometric method to study the composition of the vapor above silicon carbide. Since then, other Knudsen effusion studies have been reported.[8−12] Behrens and Rinehart[13] carried out both Knudsen effusion and Langmuir vaporization studies of SiC and concluded that the vaporization coefficients for Si(g) and SiC_2(g) above solid SiC are 1.5×10^{-3} and 8.1×10^{-3}, respectively, at 2350 K, if there are no entropy barriers for the kinetically-slow step in the vaporization process.

Drowart et al.[7] and Verhaegen et al.[11] used SiC samples in graphite Knudsen cells which guaranteed unit activity of graphite; however, the respective sample-to-orifice area ratios were reported as ≥1000 and 5−125, respectively. These uncertain or low ratios, presumably at the beginning of the experiment, would not guarantee equilibrium conditions for Si(g), according to the measurements of Behrens and Rinehart.[13] Other investigators[8−10,12] utilized pure silicon samples placed in a graphite Knudsen cell. Behrens and Rinehart[13] report a possible problem with their pressure calibration and therefore could not carry out a reliable thermodynamic evaluation of their data.

In the present investigation, new experimental data are reported for several Si_xC_y species. New Gibbs energy and heat content functions, based on recent spectroscopic and theoretical results from literature, have been evaluated. These thermal functions are combined with the experimental equilibrium data to obtain atomization enthalpies and enthalpies of formation for the molecules SiC_2, Si_2C, Si_2C_2, and Si_3C.

Thermal Functions

The structures of the silicon carbide clusters used in the thermal function evaluations are summarized in Figure 1, and both Gibbs energy (GEF_0) and heat content (HCF_0) functions are listed in Table 1. In all cases, the harmonic-oscillator rigid-rotor approximation was used.[14] Brief discussions on each of the clusters follow.

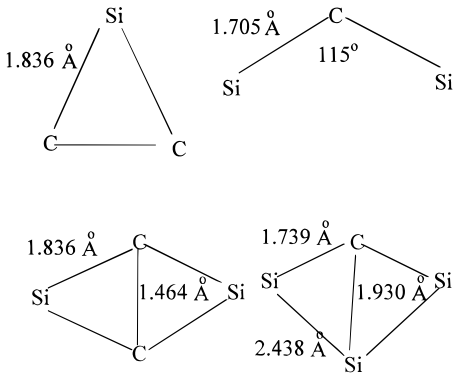

Figure 1. Structures used in the evaluation of the Gibbs energy functions and heat content functions listed in Table 1.

TABLE 1: Gibbs Energy Functions (GEF_0) in J K^{-1} mol^{-1} and Heat Content Functions (HCF_0) in kJ mol^{-1} for Gaseous SiC_2, Si_2C, Si_2C_2, and Si_3C

		T (K)			
species	type[a]	298.15	1600	2000	2400
SiC_2	GEF_0	212.5	286.5	297.7	307.2
	HCF_0	11.58	79.76	102.4	125.3
Si_2C	GEF_0	224.7	300.6	312.2	321.8
	HCF_0	11.76	81.89	104.8	127.8
Si_2C_2	GEF_0	226.5	322.8	338.7	352.0
	HCF_0	13.11	111.8	144.4	177.3
Si_3C	GEF_0	245.5	349.1	365.6	379.5
	HCF_0	14.43	116.6	150.3	184.9

[a] The reference pressure is 1.0 atm.

SiC_2. The $^1A_1$ C_{2v} structure reported by Bredohl et al.[15] was used in the GEF_0/HCF_0 evaluation; this structure is consistent with other experimental results.[16,17] Vibrational frequencies of $\nu_1 = 1746.0$, $\nu_2 = 840.6$, and $\nu_3 = 196.37$ cm^{-1} were taken from Butenhoff and Rohlfing.[18] These frequencies are consistent with gas phase[19,20] and matrix isolation spectra.[21] A singlet electronic ground state and an excited electronic state, $^1B_2$ at 20 085 cm^{-1},[15] were also considered in the thermal function evaluation, which are consistent with earlier spectroscopic results.[17,20,22−27]

Si_2C. The corrected TZ+2P+f CISD structure of Si_2C (bent geometry) by Bolten et al.[28] was adopted. This structure is consistent with other ab initio studies.[29−32] The Si−C−Si bond

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angle predicted by Bolten et al. (115°) is also consistent with the theoretical value of 118°, predicted by Sabin et al.[31] and the suggested spectroscopic value of >110° by Kafafi et al.[33] Ground state vibrational frequencies of $\nu_1 = 839.5$, $\nu_2 = 166$, and $\nu_3 = 1188.4$ cm^{-1} were used.[34] The bending mode, ν_2, was not directly measured. Presilla-Marquez and Graham[34] believe that an absorption feature at 1354.8 cm^{-1} is due to a $\nu_2 + \nu_3$ combination band from which they suggest a frequency of 166 cm^{-1} for ν_2; this value is supported by ab initio predictions.[28−30] A singlet $^1A_1$ electronic ground state was assumed for Si_2C, which is consistent with ab initio predictions.[28,30] No other electronic states are predicted to lie within 2 eV of the ground state,[31,32] and so no low-lying excited states were considered.

Si_2C_2. A D_{2h} cyclic planar structure is predicted by Lammertsma and Güner[35] to be the ground state geometry of Si_2C_2. This geometry is also consistent with the predictions from other ab initio calculations.[36,37,56] Presilla-Marquez and co-workers[37] report two experimental vibrational frequencies for the rhombus structure of Si_2C_2, $\nu_3(b_{1u}) = 982.9$ cm^{-1} and $\nu_4(b_{2u}) = 382.2$ cm^{-1}. The four remaining frequencies are the product of the predicted value from the ab initio calculations of Presilla-Marquez et al.[37] and a scaling factor of 0.967. The scaling factor was computed by comparing the two experimental frequencies with the corresponding theoretical values of 1011 and 397 cm^{-1}. The predicted singlet ^1A_g electronic ground state for Si_2C_2[35,36,56] was used. The bond lengths are from Presilla-Marquez et al.[37]

Si_3C. A planar cyclic structure was assumed for Si_3C which is based on an ab initio study by Rittby.[38] Presilla-Marquez and Graham[39] report five experimental vibrational frequencies (in cm^{-1}) for Si_3C which are $\nu_1(a_1) = 658.2$, $\nu_2(a_1) = 511.8$, $\nu_3(a_1) = 309.5$, $\nu_5(b_2) = 1101.4$, and $\nu_6(a_1) = 357.6$, and all five frequencies were used in the thermal function evaluation. The sixth frequency used, $\nu_4(b_1) = 184$ cm^{-1}, is predicted by MBPT(2) calculations[38]. An $^1A_1$ singlet electronic ground state with no low-lying electronic states was assumed.

Experimental Section

The objective of this investigation was to measure the equilibrium partial pressures of SiC_2 and other Si_xC_y species in a situation where the ratio of the Si−C sample surface area would greatly exceed the orifice area throughout the measurements. In previous studies, the sample-to-orifice area was either not reported or only at the beginning of the experiment. In the present investigation, the sample-to-orifice area was therefore evaluated at the end, as well as at the beginning of the experiments.

A magnetic focusing mass spectrometer with a Knudsen effusion cell was used. The technique and experimental procedure are described elsewhere.[40] The energy of the ionizing electrons was 11.5 eV, the emission current was 1.0 mA, and the accelerating potential was 4.5 kV. The potential on the first dynode of the detector was 2.5 kV. All temperatures were measured with a calibrated optical pyrometer, focused onto a blackbody cavity at the bottom of the graphite Knudsen cell.

The sample consisted of a mixture of 178.3 mg of 180 mesh SiC granules (NBS Standard Reference material 112b), 81.8 mg of ultra graphite powder, and 26.8 mg of silver needles (99.999% purity). The graphite powder was added to ensure unit activity of graphite. The sample was placed into a high-density (1.90 g cm^{-3}) graphite Knudsen cell with an orifice diameter of 0.51 mm. After all data were collected, the sample was reweighed with the resulting mass being 247.0 mg; therefore, at least 165 mg of SiC remained since the silver had been evaporated.

We measured the surface area of the SiC granules to be 0.117 ± 0.015 m^2 g^{-1} and so the ratio of surface area of SiC to orifice area ranged from 104 000 at the beginning to ≥95 000 at the end of the experiment. The uncertainty for both ratios is 16%.

The effective surface to orifice area was estimated according to the procedure outlined by Rosenblatt[41] as 10 000 using $\alpha = 1.5 \times 10^{-3}$ for Si(g)[13] and 4000 for SiC_2 with $\alpha = 8.1 \times 10^{-3}$.[13] This results in a possible deviation of the measured pressure from the true equilibrium pressure of approximately 7 and 3 % for Si and SiC_2, respectively. Similar possible deviations may be assumed for the other silicon carbide clusters.

After completion of the silver calibration, but before collection of the Si_xC_y data, several minor impurities were detected, which included Fe^+, Ca^+, Al^+, and SiO^+, while both Cr^+ and Co^+ were suspected; the temperature was 1700−1750 K. No Mg, V, or Ti was detected. The $^{56}Fe^+$, $^{40}Ca^+$, and $^{52}Cr^+$ ions are of particular importance since they overlap with the most abundant isotopes of Si_2, SiC, and SiC_2, respectively. Therefore, the sample was allowed to bake out at 1700−1750 K, until the Fe, Ca, and Cr had disappeared; this required about 5 h.

The measured ion currents are listed in Table 2, and the pressure constant data are listed in Table 3.

The pressure constant, $k(^{107}Ag^+)$, was determined by comparing the $^{107}Ag^+$ ion currents to the partial pressure of silver[48] for 17 $^{107}Ag^+$ ion current measurements over a temperature range of 1088−1203 K, resulting in $k(^{107}Ag) = 333 \pm 24$ atm A^{-1} K^{-1} at an ionizing electron energy of 12.3 eV; the corresponding value at 11.5 eV, the energy used in the $Si_xC_y^+$ intensity measurements, is $k(^{107}Ag) = 416 \pm 30$ atm A^{-1} K^{-1}. The pressure constant was also evaluated using the Ag/Ag_2 equilibrium,[42] where the dissociation energy[43] for Ag_2 is 158 kJ mol^{-1} and the relative ionization cross section, $\sigma(Ag_2^+)/\sigma(Ag^+)$ is 3.0.[44] The resulting value at 11.5 eV is $k(^{107}Ag) = 309 \pm 31$ atm A^{-1} K^{-1}. The two values are in fair agreement. Pressure constants for all other species are evaluated from the equation

$$k(X) = \frac{k(Ag)\,\sigma(Ag)\,\gamma(Ag)\,n(Ag)}{\sigma(X)\,\gamma(X)\,n(X)} \frac{E - A(Ag)}{E - A(X)} \qquad (1)$$

where σ, γ, n, E, and A are the maximum ionization cross section, multiplier gain, isotopic abundance, energy of the ionizing electrons, and the appearance potential, respectively; all of these quantities are listed in Table 3. The maximum ionization cross sections are from Mann;[45] molecular cross sections are assumed to be the sum of the atomic cross sections multiplied by 0.75. Multiplier gains for Si, SiC_2, and Si_2C are from earlier measurements.[46] The appearance potentials are the overall selected values[46] but are close to those measured in the present investigation, which are (in eV) Si_2 (7.0 ± 0.5), SiC_2 (10.4 ± 0.3), Si_2C (9.5 ± 0.5), Si_2C_2 (8.8 ± 0.5), and Si_3C (7.9 ± 0.5); the electron energy scale was calibrated against atomic silicon.[47]

Results and Discussion

Enthalpy changes are calculated for the following reactions:

$$Si(g) + 2C(s) = SiC_2(g) \qquad (2)$$

$$2Si(g) + C(s) = Si_2C(g) \qquad (3)$$

$$2Si(g) + 2C(s) = Si_2C_2(g) \qquad (4)$$

$$3Si(g) + C(s) = Si_3C(g) \qquad (5)$$

Both the second- and third-law methods are used for reactions 2 and 3 whereas only the third-law method is used for reactions 4 and 5 since there are not enough data for a reliable second-

TABLE 2: Ion Current Measurements in pA

T (K)	Si^+	SiC_2^+	Si_2C^+	Si_2^+	Si_3C^+	$Si_2C_2^+$
1757	0.21		0.01			
1780	0.27		0.008			
1817	0.53	0.008	0.036			
1839	0.74	0.012	0.050			
1861	1.21	0.020	0.091			
1891	2.35	0.040	0.17			
1879	1.47	0.020	0.11			
1905	2.10	0.045	0.17			
1913	2.82	0.062	0.26			
1935	3.47	0.081	0.34			
1906	2.21	0.053	0.20			
1937	3.13	0.071	0.30			
1954	4.72	0.12	0.46			
1982	7.58	0.20	0.72			
2012	11.4	0.44	1.40	0.15	0.012	
1983	7.63	0.22	0.79	0.059		
1962	5.97	0.18	0.49	0.051		
1981	5.20	0.18	0.53	0.043		
1987	7.92	0.29	0.81	0.097		
2021	11.7	0.52	1.55	0.12	0.008	
2048	16.8	0.77	2.00	0.18	0.013	
2073	23.1	1.22	3.13	0.20	0.021	
2040	11.1	0.53	1.23	0.11		
1849	0.50	0.01	0.027			
1879	0.82	0.019	0.049			
1828	0.31	0.005	0.016			
1866	0.81	0.016	0.045			
1894	1.28	0.043	0.087			
1927	1.89	0.052	0.16			
1954	3.12	0.099	0.28			
1969	5.44	0.20	0.51	0.033		
1954	3.84	0.11	0.34	0.020		
1945	2.66	0.078	0.21	0.017		
1971	4.55	0.19	0.44	0.033		
1985	6.63	0.28	0.73	0.053		
2015	11.3	0.52	1.27	0.096	0.014	
2063	16.9	0.84	2.11	0.13		
2013	11.6	0.55	1.60	0.082	0.008	
2050	15.0	0.74	2.14	0.13	0.015	0.009
2024	11.0	0.51	1.47	0.087	0.011	0.004
2055	17.8	0.88	2.57	0.14	0.015	0.008
2080	21.3	1.10	3.23	0.17	0.023	0.012
2056	21.0	1.17	2.94	0.12	0.021	0.009
2040	17.0	0.83	2.45	0.11	0.021	0.010
2063	21.9	1.23	3.32	0.16	0.026	0.016
1825	0.52		0.027			
1808	0.48		0.016			
1793	0.41		0.016			
1878	2.27	0.046	0.11			
1934	4.12	0.11	0.30			
1991	7.02	0.22	0.55	0.037		
2024	8.77		0.85	0.065		

TABLE 3: Pressure Constants and Related Data

species	σ(max)	γ/γ_{Ag}	*n*	AP[e] (eV)	*k* (atm A^{-1} K^{-1})
Ag	5.05	1.00	0.518	7.57[a]	416
Ag_2	15.1	(1.0)[b]	0.499	7.3 ± 0.3[c]	135
Si	5.35	1.7	0.922	8.15[a]	152
Si_2	8.03	(1.7)	0.850	7.5 ± 0.4[d]	92
SiC_2	6.98	1.4	0.902	10.1 ± 0.3[d]	347
Si_2C	9.51	2.0	0.841	9.4 ± 0.3[d]	127
Si_2C_2	11.0	(1.7)	0.832	8.0 ± 0.3[d]	79
Si_3C	13.5	(2.0)	0.775	8.3 ± 0.4[d]	64

[a] Reference 47. [b] Estimated values are in parentheses. [c] Reference 43. [d] Reference 46. [e] Appearance potential.

law evaluation. In the evaluation of atomization enthalpies and enthalpies of formation, the heats of vaporization for atomic carbon and silicon were taken from Hultgren et al.[48]

In arriving at the overall errors in the third-law values, we followed the procedure given by Schmude et al.[49] but increased the estimated error in temperature to ±20 K and added a 10% uncertainty to the partial pressures due to possible effects of low vaporization coefficients.

SiC_2. The second-law enthalpy change for reaction 2 is $\Delta H_{rxn,1940} = 165 \pm 9$ kJ mol^{-1}, and the corresponding values at 0 and 298 K are 178 ± 9 and 180 ± 9 kJ mol^{-1}. The second-law entropy change is $\Delta S_{1940} = 62 \pm 5$ or $\Delta S_{298} = 75 \pm 5$ J K^{-1} mol^{-1}. The uncertainties are standard deviations.

The third-law enthalpy change for reaction 2 is $\Delta H_{rxn,0} = 173 \pm 2$ or $\Delta H_{rxn,298} = 175 \pm 2$ kJ mol^{-1}, and the entropy change is $\Delta S_{298} = 72$ J K^{-1} mol^{-1}.

The selected enthalpy change for reaction 2 is $\Delta H_{rxn,0} = 176 \pm 7$ or $\Delta H_{rxn,298} = 178 \pm 7$ kJ mol^{-1}, based on the average of the second- and third-law values. The atomization enthalpy for $SiC_2(g)$ is $\Delta H_{a,0} = 1247 \pm 8$ or $\Delta H_{a,298} = 1256 \pm 8$ kJ mol^{-1} and the enthalpy of formation is $\Delta H_{f,0} = 627 \pm 9$ or $\Delta H_{f,298} = 633 \pm 9$ kJ mol^{-1}.

The atomization enthalpy for SiC_2 reported here is lower than the value suggested by Verhaegen et al.[11] ($\Delta H_{a,0} = 1268 \pm 25$ kJ mol^{-1}) and the value deduced from the reaction sequence $SiC_2(g) = Si(g) + C_2(g)$ and $C_2(g) = 2C(g)$, ($\Delta H_{a,0} = 1293 \pm 30$ kJ mol^{-1}) reported by Drowart et al.[7] The enthalpy of formation reported here is higher than the value selected from refs 7, 9, and 11 by Chase et al.[50] ($\Delta H_{f,0} = 609 \pm 29$ kJ mol^{-1}). These discrepancies suggest that the atomization enthalpy for SiC_2 is 20−50 kJ mol^{-1} lower than previously reported. McMichael Rohlfing[51] used both the QCISD/6-31G(d) and the QCISD/6-311+G(3df) methods to predict binding energies of 1136 and 1158 kJ mol^{-1} for SiC_2 which are 91 and 93% of our experimental value. The good second- and third-law agreement for SiC_2 along with the lack of a temperature trend in the third-law data suggests that the harmonic-oscillator rigid-rotor approximation for the large-amplitude vibration of SiC_2[52] is a reasonable approximation.[53] This is not the case, however, for C_3.[54] The differences between the SiC_2 and C_3 studies are (a) The SiC_2 data were obtained at around 1800−2100 K, which is 500 K lower than the temperatures at which the C_3 data were measured, and (b) the frequency of the large-amplitude vibration for SiC_2 (180 cm^{-1}) is almost 3 times that of C_3. These two factors are believed to be the reason for the satisfactory performance of the harmonic-oscillator rigid-rotor approximation for SiC_2.

Si_2C. The second-law enthalpy change for reaction 3 is $\Delta H_{rxn,1926} = -358 \pm 15$, $\Delta H_{rxn,0} = -340 \pm 15$, or $\Delta H_{rxn,298} = -344 \pm 15$ kJ mol^{-1}. The second-law entropy change is $\Delta S_{1926} = -92 \pm 7$ or $\Delta S_{298} = -76 \pm 7$ J K^{-1} mol^{-1}. The uncertainties are standard deviations.

The third-law enthalpy change for reaction 3 is $\Delta H_{rxn,0} = -342 \pm 4$ or $\Delta H_{rxn,298} = -346 \pm 4$ kJ mol^{-1}; the corresponding entropy change is $\Delta S_{298} = -77$ J K^{-1} mol^{-1}.

The average of the second- and third-law enthalpies for reaction 3 is $\Delta H_{rxn,0} = -341 \pm 10$ or $\Delta H_{rxn,298} = -345 \pm 10$ kJ mol^{-1}. The resulting atomization enthalpy for gaseous Si_2C is $\Delta H_{a,0} = 1052 \pm 10$ or $\Delta H_{a,298} = 1062 \pm 10$ kJ mol^{-1} while the corresponding enthalpy of formation is $\Delta H_{f,0} = 562 \pm 11$ or $\Delta H_{f,298} = 566 \pm 11$ kJ mol^{-1}.

The present atomization enthalpy of Si_2C is lower than the value selected by Verhaegen et al.[11] ($\Delta H_{a,0} = 1071 \pm 25$ kJ mol^{-1}) but is close to the value deduced from the reaction sequence $Si_2C(g) = Si_2(g)+C(g)$ and $Si_2(g) = 2Si(g)$, ($\Delta H_{a,0} = 1046 \pm 30$ kJ mol^{-1}) reported by Drowart et al.[7] The present enthalpy of formation is higher than the value selected from refs 7, 9, and 11 by Chase et al.[50] ($\Delta H_{f,0} = 531.7 \pm 25$ kJ mol^{-1}). Rittby[52] calculated atomization enthalpies of 1013 and 994 kJ mol^{-1} for Si_2C at the MBPT[2]/6-31G* and MBPT[4]/6-31G* levels which are 96 and 94% of our experimental value.

Si_2C_2. The third-law enthalpy change for reaction 4 is $\Delta H_{rxn,0} = 230 \pm 4$ or $\Delta H_{rxn,298} = 234 \pm 4$ kJ mol^{-1}; the uncertainties are standard deviations. The atomization enthalpy for gaseous Si_2C_2 is $\Delta H_{a,0} = 1652 \pm 14$ or $\Delta H_{a,298} = 1667 \pm 14$ kJ mol^{-1}. The enthalpy of formation for Si_2C_2 is $\Delta H_{f,0} = 673 \pm 15$ or $\Delta H_{f,298} = 678 \pm 15$ kJ mol^{-1}.

The present atomization enthalpy is higher than the one calculated from the reaction sequence $Si_2C_2(g) = 2SiC(g)$; $2SiC(g) = 2Si(g) + 2C(g)$ ($\Delta H_{a,0} = 1628 \pm 36$ kJ mol^{-1}) by Drowart et al.[7] Rittby[53] has calculated atomization enthalpies of 1592 and 1544 kJ mol^{-1} for Si_2C_2 at the MBPT[2]/6-31G* and MBPT[4]/6-31G* levels which are 96 and 94%, of our experimental value.

Si_3C. The third-law enthalpy change for reaction 5 is $\Delta H_{rxn,0} = -725 \pm 4$ or $\Delta H_{rxn,298} = -735 \pm 4$ kJ mol^{-1}, where the uncertainties are standard deviations. The atomization enthalpy for Si_3C is $\Delta H_{a,0} = 1437 \pm 14$ or $\Delta H_{a,298} = 1451 \pm 14$ kJ mol^{-1} while the enthalpy of formation for Si_3C is $\Delta H_{f,0} = 629 \pm 15$ or $\Delta H_{f,298} = 632 \pm 15$ kJ mol^{-1}.

The present atomization enthalpy is higher than the value calculated by Drowart et al.[7] from the reaction sequence $Si_3C(g) = Si_2(g) + SiC(g)$; $Si_2(g) = 2Si(g)$; $SiC(g) = Si(g) + C(g)$ ($\Delta H_{a,0} = 1392 \pm 36$ kJ mol^{-1}). The MBPT[2]/6-31G* and MBPT[4]/6-31G* atomization enthalpies for Si_3C, calculated by Rittby,[53] are 1380 and 1341 kJ mol^{-1}, which are 96 and 93%, of our experimental value.

Conclusions

A Knudsen effusion mass spectrometric investigation has been carried out on small silicon carbide clusters. The experimental data have been combined with new thermal functions based on recent experimental and theoretical work. The resulting atomization enthalpies, $\Delta H_{a,0}$, for SiC_2, Si_2C, Si_2C_2, and Si_3C are 1247 ± 8, 1052 ± 10, 1652 ± 14, and 1437 ± 14 kJ mol^{-1}, respectively. The enthalpies of formation, $\Delta H_{f,298}$, are 633 ± 9, 566 ± 10, 678 ± 15, and 632 ± 15 kJ mol^{-1} for SiC_2, Si_2C, Si_2C_2, and Si_3C, respectively. There is generally a difference of 20−50 kJ mol^{-1} between the values reported here and those reported in previous studies. Much of this discrepancy is due to the assumption of linear structures for the small silicon carbon clusters, made in previous studies; low vaporization coefficients may have also influenced previous results. The most recent theoretical atomization energies are between 91 and 96% of the experimental values.

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