Electronic Structure and Thermodynamic Properties of the Molecule GeC from All-Electron *ab Initio* Calculations and Knudsen Effusion Mass Spectrometric Measurements

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All-electron *ab initio* multiconfiguration self-consistent-field (CASSCF) and multireference configuration interaction (MRCI) calculations have been carried out to determine the low-lying states of the molecule GeC. The electronic ground state is predicted to be $^3\Pi$. Based on the results of the MRCI calculations, the equilibrium distance for the $^3\Pi$ ground state has been computed as 1.842 Å and the vibrational frequency as 827 cm^{-1}. The ground state is separated from the excited states $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ by 3552, 5768, 7322, and 8303 cm^{-1}, respectively. The chemical bond in the $^3\Pi$ electronic ground state has double-bond character. It is polar with charge transfer from Ge to C giving rise to a dipole moment of 1.68 D at 1.84 Å. Thermal functions as derived from the theoretical molecular parameters were used in the calculation of the thermodynamic properties of the GeC molecule from new mass spectrometric equilibrium data. Also, the literature value for the dissociation energy of GeC has been reevaluated. The recommended dissociation energy, D°_0(GeC), and enthalpy of formation, $\Delta_f H^\circ_{298.15}$(GeC), in kJ mol^{-1} are 455.7 ± 11 and 630.4 ± 11, respectively.

Introduction

There has been renewed interest in germanium−carbon alloys due to their interesting semiconductor properties, such as the apparent tunability of the energy gap over a wide range between that of silicon and germanium.[1−4] As thin films containing germanium and carbon are formed by vapor deposition methods, it is important to understand the bonding in molecules containing germanium and carbon. Earlier we have reported the thermodynamic properties of gaseous germanium carbides, namely, Ge_2C, GeC_2, Ge_3C, and Ge_2C_2.[5] The present theoretical and experimental investigation of the GeC molecule is in continuation of our program to determine the thermodynamic properties of small mixed clusters containing silicon, germanium, boron, carbon, and nitrogen that are relevant to semiconductor technology.[5−9] The only report on the GeC molecule in the literature is by Drowart et al.,[10] who measured its dissociation energy by Knudsen effusion mass spectrometry.

The molecule SiC, which is isovalent with GeC, has been the subject of several theoretical and spectroscopic investigations, and it is now well established that the SiC molecule has a $^3\Pi$ ground state, and the lowest lying excited state is $^3\Sigma^-$.[11−16] Furthermore, other low-lying excited states are $^1\Pi$, $^1\Sigma^+$, and $^1\Delta$.[11,16]

Much less is known about the molecule GeC. In earlier work,[17] we have performed all-electron Hartree−Fock calculations combined with valence CI calculations to determine the low-lying states of the GeC molecule. In that work, the electronic ground state was identified as $^3\Pi$ and the lowest lying excited states as $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$. The transition energies between the $^3\Pi$ ground state and the low-lying excited states were derived as 5371, 7602, 9152, and 10 174 cm^{-1}, respectively. The equilibrium distance for the $^3\Pi$ ground state was derived as 1.847 Å and the vibrational frequency as 711 cm^{-1}.

In the present work, elaborate all-electron *ab initio* calculations of the low-lying electronic states of the GeC molecule have been performed to elucidate its nature of bonding and to obtain molecular parameters. New mass spectrometric equilibrium measurements for the GeC molecule have been carried out, and from the predicted molecular parameters, new thermal functions have been calculated to evaluate the dissociation energy and enthalpy of formation of GeC(g). The results have been combined with those of the reevaluated literature data.

Theoretical Investigations

In the present work, we have performed further investigations of the low-lying electronic states of GeC by carrying out multiconfiguration self-consistent-field (MCSCF) calculations within the complete active space self-consistent-field approach (CASSCF). In addition, the molecular orbitals determined in the CASSCF calculations have been utilized to perform multireference configuration interaction calculations (MRCI). The calculations have been performed using the program system MOLCAS, version 3.[18]

The wave functions were expanded in basis sets consisting of contracted Gaussian-type functions. For the Ge atom, we have utilized Huzinaga's (14s, 11p, 5d) basis set,[19] but the exponents of the most diffuse s and p functions have been increased slightly, and a diffuse s as well as a diffuse p function has been added. The exponents of the three most diffuse s functions in the final basis set are 0.3472, 0.1033, and 0.0369, and those of the most diffuse p functions are 0.3086, 0.1224, and 0.052. Furthermore, the basis set has been augmented with one d

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TABLE 1: Spectroscopic Constants of the Low-Lying Electronic States of the GeC Molecule as Derived from the Results of CASSCF and MRCI Calculations. (Also Shown Are the Dipole Moments)

	CASSCF calculations					MRCI calculations				
state	equilib dist, Å	vib freq, cm^{-1}	trans energy, cm^{-1}	dissoctn energy,[a] eV	dipole moment,[b] D	equilib dist, Å	vib freq, cm^{-1}	trans energy, cm^{-1}	dissoctn energy,[a] eV	dipole moment,[b] D
$^3\Pi$	1.845	841	0	3.30	1.336	1.842	827	0	3.44	1.677
$^3\Sigma^-$	1.918	727	4702	2.72	2.093	1.908	747	3552	3.00	2.331
$^1\Sigma^+$	1.758	1006	4172	2.79	2.041	1.765	943	5768	2.73	2.070
$^1\Pi$	1.854	827	8200	2.29	1.527	1.848	823	7322	2.54	1.828
$^1\Delta$	1.950	627	9764	2.09	1.842	1.938	656	8303	2.42	1.992

[a] Derived as the difference between the total molecular energy of each state at the equilibrium distance and the sum of the atomic energies obtained at the CASSCF and MRCI levels, respectively. [b] Values are derived at the equilibrium internuclear distances by interpolation.

function with exponent 0.225 347 and one f function with exponent 3.438. Using segmented contraction, the primitive basis (15s, 12p, 6d, 1f) has been contracted to (9s, 7p, 3d, 1f), resulting in triple-ζ representation of the valence orbitals 4s and 4p, as well as of the 3d orbitals. The core orbitals 1s, 2s, 3s, 2p, and 3p are represented by double-ζ functions. In addition, the basis contains an f polarization function. For the C atom, we have utilized Huzinaga's (10s, 6p) basis,[20] augmented with a d polarization function with exponent 0.75. The primitive basis (10s, 6p, 1d) has been contracted to (4s, 3p, 1d), resulting in double-ζ representations of the s functions, triple-ζ representation of the 2p orbital, and a d polarization function.

CASSCF and MRCI calculations have been performed at the internuclear distances 3.30, 3.48, 3.60, and 3.90 au for the states $^3\Pi$, $^3\Sigma^-$, $^1\Pi$, and $^1\Delta$ and at the internuclear distances 3.00, 3.30, 3.48, and 3.60 au for the $^1\Sigma^+$ state.

In the CASSCF calculations, the core orbitals, i.e., 1s, 2s, 3s, 2p, 3p, 3d of Ge and 1s of C, were kept fully occupied. All valence orbitals, i.e., 4s and 4p of Ge and 2s and 2p of C, have been included in the active space. The CASSCF calculations have been performed in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the GeC molecule. The number of configurations included in the CASSCF calculations were 592 for $^3\Pi$, 584 for $^3\Sigma^-$, 492 for $^1\Sigma^+$, 432 for $^1\Pi$, and 408 for $^1\Delta$. The molecular orbitals optimized in the CASSCF calculations have been utilized as the basis in the MRCI calculations. In the MRCI calculations, all single and double excitations were allowed from all the configurations included in the CASSCF calculations. The number of configurations included in the final CI calculations amount to 1298 183 for $^3\Pi$, 1286 962 for $^3\Sigma^-$, 772 388 for $^1\Sigma^+$, 759 256 for $^1\Pi$, and 747 848 for $^1\Delta$.

The spectroscopic constants for the GeC molecule have been derived by solving the Schrödinger equation for the nuclear motion numerically. The ensuing values based on the results of the CASSCF and MRCI calculations are reported in Table 1 together with the values for the dipole moments and for the dissociation energies. Figure 1 shows the potential energy curves as derived from the MRCI calculations. Table 2 shows the contributions of the major configurations to the MRCI wave functions for the low-lying electronic states as functions of the internuclear distance. The occupations of the natural valence orbitals for the low-lying states are reported in Table 3.

The results of the MRCI calculations show that the electronic ground state of the GeC molecule is $^3\Pi$ and that this state is well separated from the low-lying excited states, $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ by 3552, 5768, 7322, and 8303 cm^{-1}, respectively. It is noted that an interchange of the states $^3\Sigma^-$ and $^1\Sigma^+$ has occurred in the MRCI relative to the CASSCF calculations. The sequence of the low-lying electronic states of GeC is identical to that determined for the isovalent molecule SiC.[11,16] For the ground state, the equilibrium distance is estimated to be accurate to about 0.02 Å and the vibrational frequency to about 20 cm^{-1}. The transition energies between states of identical configuration, i.e., $^3\Pi$ and $^1\Pi$, and between $^3\Sigma^-$ and $^1\Delta$ are probably accurate to some hundred inverse centimeters.

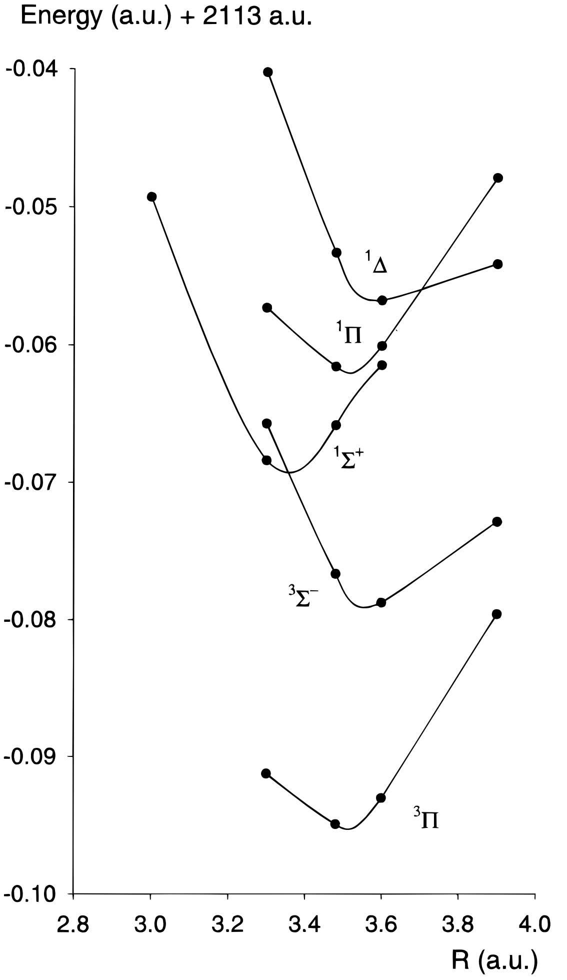

Figure 1. Potential energy curves of five low-lying electronic states of GeC as derived from MRCI calculations.

Table 2 shows that the low-lying states of GeC essentially are derived from three different configurations. Thus, the major configuration of the states $^3\Pi$ and $^1\Pi$ is $(8\sigma)^2(9\sigma)^2(10\sigma)^1(4\pi)^3$. The configuration $(8\sigma)^2(9\sigma)^2(10\sigma)^2(4\pi)^2$ is the major configuration for the states $^3\Sigma^-$ and $^1\Delta$. Finally, the major configuration of the state $^1\Sigma^+$ is $(8\sigma)^2(9\sigma)^2(4\pi)^4$, but this state also has some admixture of the configuration $(8\sigma)^2(9\sigma)^2(10\sigma)^2(4\pi)^2$. The correlation energy gained in the MRCI calculations is largest for the states $^3\Sigma^-$ and $^1\Delta$, with the largest population being in the 10σ orbital; it is smallest in the $^1\Sigma^+$ state, with the smallest population being in the 10σ orbital. This results in the interchange of the states $^3\Sigma^-$ and $^1\Sigma^+$.

TABLE 2: Contributions of the Major Configurations to the MRCI Wave Functions describing the $^3\Pi$ Ground State and the Excited States $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ of the GeC Molecule as Functions of the Internuclear Distance.

	valence shell config						contribution of valence shell config (%) at internuclear dist				
state	8σ	9σ	10σ	11σ	4π	5π	3.0 au	3.3 au	3.48 au	3.6 au	3.9 au
$^3\Pi$	2	2	1	0	3	0		82	81	79	76
$^3\Sigma^-$	2	2	2	0	2	0		87	86	85	83
$^1\Sigma^+$	2	2	0	0	4	0	75	72	66	59	
	2	2	2	0	2	0	1	4	9	13	
$^1\Pi$	2	2	1	0	3	0		83	82	81	78
$^1\Delta$	2	2	2	0	2	0		86	84	84	81

The 8σ orbital is mainly the bonding combination of the Ge 4s and C 2s orbitals. The 9σ orbital is the corresponding antibonding orbital. The 10σ orbital is the bonding combination of the Ge 4pσ and the C 2pσ, and the 11σ orbital is the corresponding antibonding orbital. Orbitals 4π and 5π are the bonding and antibonding combinations of the Ge 4pπ and the C 2pπ, respectively. Thus, for each of the low-lying states, the formal bond order is 2 in their leading configuration. Furthermore, from Table 3, it is recognized that the excess of electrons in bonding relative to antibonding valence orbitals resulting from the MRCI calculations amounts to 3.58, 3.69, 3.68, 3.63, and 3.61 e for the states $^3\Pi$, $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$, at internuclear distances close to the equilibrium distance of each state. This indicates that the chemical bond has double-bond character in all the low-lying states.

From Table 1, it is noted that the equilibrium distances of the low-lying states are found in three distinct groups. For the states $^3\Pi$ and $^1\Pi$, the equilibrium distances are 1.842 and 1.848 Å (3.48 and 3.49 au). The equilibrium distances are larger for the states $^3\Sigma^-$ and $^1\Delta$, 1.908 and 1.938 Å (3.61 and 3.66 au), respectively, and shorter for the $^1\Sigma^+$ state, 1.765 Å (3.34 au). It appears that the number of electrons in the 4π orbitals is correlated with the bond length. Thus, at 3.48 au, the populations of the 4π orbitals are 2.79 and 2.81 e for the states $^3\Pi$ and $^1\Pi$. For the states $^3\Sigma^-$ and $^1\Delta$, the corresponding populations are 1.93 and 1.89 e at 3.60 au. Finally, the state $^1\Sigma^+$ has a population of 3.59 e in the 4π orbitals at 3.30 au. Thus, the more electrons in the 4π orbital, the shorter the bond.

In all the low-lying states, charge is transferred from Ge to C. This results in a gross atomic charge of +0.23 e on Ge in the $^3\Pi$ ground state and of +0.20 e in the state $^1\Pi$, both at the internuclear distance 3.48 au. The gross atomic charges in the states $^3\Sigma^-$ and $^1\Delta$ amount to +0.18 and +0.15 e, respectively, at 3.60 au. At 3.30 au, the gross atomic charge on Ge in the $^1\Sigma^+$ state amounts to +0.24 e.

The states $^3\Pi$ and $^1\Pi$ resemble each other closely. They essentially represent the triplet and the singlet spin couplings of the angular momenta of the electrons in the singly occupied orbitals 9σ and 4π. Likewise, the states $^3\Sigma^-$ and $^1\Delta$ are basically different couplings of the space and spin angular momenta of the singly occupied 4π orbitals. The major configuration of the states $^3\Sigma^-$ and $^1\Delta$, $(8\sigma)^2(9\sigma)^2(10\sigma)^2(4\pi)^2$, also gives rise to a state of $^1\Sigma^+$ symmetry, but it is noted that the major configuration of the lowest lying $^1\Sigma^+$ state is $(8\sigma)^2(9\sigma)^2(4\pi)^4$, although it has some admixture of the configuration $(8\sigma)^2(9\sigma)^2(10\sigma)^2(4\pi)^2$.

The predicted dissociation energy, $D_e = 3.44$ eV, corresponds to a value of $D_0 = 3.39$ eV. This represents 74% of the experimental value of 4.72 eV obtained in the present investigation. The discrepancy between the calculated and the experimental dissociation energies is probably mostly due to the lack of correlation of the 3d electrons of Ge.

Mass Spectrometric Measurements

The mass spectrometric measurements were performed following the measurements of the germanium carbide clusters by Schmude et al.[5] in series 2, under conditions where unit activity of germanium in the condensed phase was not ascertained anymore. The energy of the ionizing electrons was 11 eV. Other experimental details are given in ref 5.

The vapor species were identified from their mass-to-charge ratios and isotopic abundances. Table 4 gives the measured ion intensities pertinent to the present study, namely, Ge^+, Ge_2^+, GeC^+, GeC_2^+, and Ge_2C^+. The ion intensities of all the species except for GeC^+ are those corresponding to the most abundant isotope. For GeC^+, the ion intensities were measured at mass 84 to avoid a possible contribution of any residual gaseous GeO to the ion intensity at mass 86. As the ion intensities were recorded at 11 eV, the fragmentation contribution to the GeC^+ intensity from either Ge_2C or GeC_2 is considered negligible, because fragmentation to GeC^+ sets in at an energy of 15 eV.[10]

The Gibbs energy functions, $-(G_T - H_0)/T$, and enthalpy increments, $H_T - H_0$, needed in the evaluation of the reaction enthalpies were taken from the literature for Ge_2(g),[21] Ge(g),[22] C(s),[23] Ge_2C(g),[5] and GeC_2.[5] Those for GeC(g) were computed according to statistical thermodynamic procedures, using the harmonic oscillator, rigid rotator approximation,[24] and the molecular constants obtained from the MRCI calculations (Table 1) in the present investigation. At the respective temperatures 298.15, 1600, 1800, 2000, 2200, and 2400 K, the $-(G_T - H_0)/T$ values, in J mol^{-1} K^{-1}, are 208.9, 263.2, 267.4, 271.1, 274.6, and 277.8 and the $H_T - H_0$ values, in kJ mol^{-1}, are 8.86, 56.50, 64.38, 72.36, 80.40, and 88.50, respectively. The thermal functions for Ge_2(g),[21] Ge_2C(g),[5] and GeC_2(g)[5] have been adjusted to correspond to the standard pressure $p° = 1$ bar instead of $p° = 1$ atm.

The measured ion currents, I_i (Table 4), were related to the corresponding partial pressures, P_i, according to the relation $P_i = k_i I_i T$. The reference calibration constant, $k_{Ge} = 0.10 \pm 0.03$ bar A^{-1} K^{-1}, has been determined as described earlier[25] using the equilibrium $Ge_2(g) = 2Ge(g)$ with $D°_0(Ge_2) = 260.4 \pm 7.0$ kJ mol^{-1}.[21] The k_i values for the other species were then calculated employing the relation $k_i = k_{Ge}(\sigma\gamma n_i)_{Ge}/(\sigma\gamma n_i)_i$. The ionization cross sections, σ_i, of Ge_2 and the germanium carbide molecules were assumed to be equal to 0.75 times the sum of the atomic cross section from Freund et al.[26] for Ge(g) and from Mann[27] for C(g) at the corresponding electron impact energies. The multiplier gains, γ_i, for the germanium-containing ionic species were taken to be the same as that for Ge^+. The isotopic abundances, n_i, of the atomic species were taken from De Bievre and Barnes.[28] The resulting pressure constants and related data are given in footnote *b* to Table 4.

For the determination of the enthalpy of formation and dissociation energy of the GeC molecule, the enthalpy changes for the reactions

$$GeC(g) = Ge(g) + C(graph.) \quad (1)$$

$$2GeC(g) = GeC_2(g) + Ge(g) \quad (2)$$

$$GeC(g) + Ge(g) = Ge_2C(g) \quad (3)$$

were evaluated according to the third-law method using the relation $\Delta_R H°_0 = -RT \ln K_p - T\Delta\{(G_T - H°_0)/T\}$. Reaction 1 is pressure independent and assumes the graphite to be at unit

TABLE 3: Occupations in the Natural Orbitals for the Low-Lying Electronic States of GeC as Derived in MRCI Calculations[a]

state	internuclear dist, au	dipole moment, D	gross atomic charge on Ge	population in					
				8σ (C s + Ge s)	9σ (C s − Ge s)	10σ (σ)	11σ (σ^*)	4π (π)	5π (π^*)
$^3\Pi$	3.48	1.676	0.23	1.96	1.90	1.00	0.04	2.79	0.23
$^3\Sigma^-$	3.60	2.336	0.18	1.96	1.92	1.91	0.05	1.93	0.14
$^1\Sigma^+$	3.30	2.069	0.24	1.96	1.81	0.25	0.02	3.59	0.29
$^1\Pi$	3.48	1.822	0.20	1.96	1.90	1.00	0.04	2.81	0.20
$^1\Delta$	3.60	1.986	0.15	1.96	1.92	1.91	0.05	1.89	0.18

[a] Also shown are the dipole moments and the gross atomic charges on Ge at the respective internuclear distances.

TABLE 4: Measured Ion Intensity Data of Ge^+, Ge_2^+, GeC^+, GeC_2^+, and Ge_2C^+[a,b]

T, K	I_{Ge^+}, 10^{-8} A	I_{Ge_2}, 10^{-11} A	I_{GeC^+}, 10^{-12} A	$I_{GeC_2^+}$, 10^{-10} A	$I_{Ge_2C^+}$, 10^{-11} A
2033	3.85	3.78	4.8	0.56	0.88
2070	6.49	5.28	8.7	1.25	1.33
2054	6.28	4.29	9.3	1.36	1.00
2036	3.74	1.67	6.0	0.67	0.49
2044	2.54	1.05	3.0	0.40	

[a] The ion intensity of GeC was measured at mass 84; all other intensities are for the maximum intensity peaks. [b] $k_{Ge} = 0.10 \pm 0.03$, $k_{Ge_2} = 0.10$, $k_{GeC} = 0.18$, $k_{GeC_2} = 0.14$, and $k_{Ge_2C} = 0.10$ (bar A^{-1} K^{-1}). $n_{Ge} = 0.3656$, $n_{Ge_2} = 0.2382$, $n_{GeC} = 0.2710$, $n_{GeC_2} = 0.3593$, and $n_{Ge_2C} = 0.2361$. $\sigma_{Ge_xC_y} = 0.75(x\sigma_{Ge} + y\sigma_C)$, $\sigma_{Ge} = 2.34$, and $\sigma_C = 0$.

TABLE 5: Third Law Enthalpy of Reactions, $\Delta_rH°_0$ in kJ mol^{-1}, at Each Temperature for Reactions 1−3[a]

	T, K	$\Delta_rH°_0$		
		R1	R2	R3
present work	2033	−252.5	−276.0	−453.4
	2070	−255.6	−283.4	−449.5
	2054	−252.0	−279.9	−440.6
	2036	−248.6	−271.6	−440.9
	2044	−254.7	−280.8	
ref 10	1860	−254.4	−272.1	−439.1
	1765	−250.6		−437.9
	1810	−269.1	−310.0	
	1920	−259.0	−284.4	−445.7

[a] The reevaluated data from ref 10 are also included.

TABLE 6: Average Third Law Enthalpy of Reactions, $\Delta_rH°_0$ in kJ mol^{-1}, and Enthalpy of Formation, $\Delta_fH°_0$, of GeC Derived from Them[a]

reaction	present work		ref 10	
	$\Delta_rH°_0$	$\Delta_fH°_0$	$\Delta_rH°_0$	$\Delta_fH°_0$
1	−252.7 ± 2.7	624.4	−258.3 ± 8.0	630.0
2	−278.4 ± 4.6	620.2	−288.8 ± 19.3	625.4
3	−446.1 ± 6.4	624.2	−440.9 ± 4.2	619.0

[a] The reevaluated data from ref 10 are also included. Standard deviation of the mean (see Table 5).

activity, reaction 2 is an all-gas-phase pressure-independent reaction, and reaction 3 is an all-gas-phase reaction and pressure dependent. The reaction enthalpies at each temperature of measurement are given in Table 5, and the average derived from them for each reaction is given in Table 6.

The average enthalpies of formation derived from the reaction enthalpies are also given in Table 6. The necessary enthalpies of formation for C(g),[23] $\Delta_fH°_0 = 711.2 \pm 0.5$ kJ mol^{-1}, and for Ge(g),[29] $\Delta_fH°_0 = 371.7 \pm 2.1$ kJ mol^{-1} were taken from the literature. Those for Ge_2C and GeC_2 in ref 5 were reevaluated to comply with the different cross-section assumptions adopted in the present investigation for Ge[26] and C:[27] series 1, at 14 eV, $\sigma_{Ge} = 4.46$ Å^2 and $\sigma_C = 0.477$ Å^2. The reevaluation of the intensity−temperature data in ref 5 yielded $\Delta_fH°_{298.15}$, in kJ mol^{-1}, of 594.8 ± 10 (601 ± 10) for GeC_2 and 552.6 ± 12 (554 ± 12) for Ge_2C. The values previously reported are given in parentheses.

There is good agreement among the $\Delta_fH°_0$ values derived from these three different reactions. This shows that the data for Ge(g), GeC_2(g), and Ge_2C(g) are consistent with those in ref 5, and it gives additional proof for the absence of a fragmentation contribution to I (GeC^+) from both GeC_2 and Ge_2C at the 11-V electron impact energy used in the experiments.

The selected values from the present investigation of $\Delta_fH°_0$(GeC,g) = 624.4 ± 11 kJ mol^{-1} and $D°_0$(GeC) = 458.4 ± 11 kJ mol^{-1} were based on reaction 1 only, since reactions 2 and 3 do not provide independent determinations of these properties. Here the overall uncertainty was determined as described elsewhere,[30] by taking into consideration the estimated uncertainty in the temperature (±10 K), partial pressures (50%), relative multiplier gains (30%), and free-energy functions (2 J K^{-1} mol^{-1}).

Drowart et al.[10] in their mass spectrometric investigation of gaseous germanium carbides employed the ionization cross-section data from Otvos and Stevenson[31] and the partial pressure data of Ge(g) in equilibrium over Ge(l) from Stull and Sinke[32] for obtaining the pressure calibration constants. The partial pressures given at 1860 K above the germanium−graphite and at 1810 and 1920 K above the germanium−silicon carbide−graphite systems were reevaluated to derive the enthalpies of reactions 1−3. The germanium in the Ge−Si−graphite system is not at unit activity; therefore, the data point at 1765 K was not considered for the pressure-dependent reaction (3), due to lack of original data to correct for the pressure calibration constant.

The partial pressures given in ref 10 were revised by correcting them for the difference in the ionization cross sections and the partial pressure of Ge(g) over Ge(l) used in ref 10 and those from ref 29 employed in the present study according to the following relations:

$$(p_{Ge})_{revised} = (p_{Ge})_{ref10}[(p_{Ge})_{ref29}/(p_{Ge})_{ref32}] \tag{4}$$

$$(p_{Ge}/p_{GexCy})_{revised} = (p_{Ge}/p_{GexCy})_{ref10}[(\sigma_{Ge}/\sigma_{GexCy})_{ref10}/(\sigma_{Ge}/\sigma_{GexCy})_{present}] \tag{5}$$

The ratio of p_{Ge}/p_{GeC} employed in the reevaluation was 1.873 × 10^4 (1860 K), 3.335 × 10^4 (1765 K), 7.645 × 10^4 (1810 K), and 1.538 × 10^4 (1920 K). Here an average electron impact energy of 13.5 eV[10] has been used in correcting for the energy dependence of the cross sections of Ge[26] and C.[27] The individual $\Delta_rH°_0$ values derived from the reevaluated data are listed in Table 5, and the average reaction enthalpies and enthalpy of formation derived from them are included in Table 6. The values agree well with the corresponding ones from the present investigation. The average enthalpy of formation, $\Delta_fH°_0$(GeC,g) = 630.0 kJ mol^{-1} was derived from the enthalpy of reaction 1 (Table 6). The corresponding dissociation energy is $D°_0$(GeC) = 452.9 kJ mol^{-1}. The dissociation energy as reported by Drowart et al.[10] was 456 ± 21 kJ mol^{-1}.

The reevaluated results from Drowart et al.[10] have been combined with those from the present investigation to obtain an assessed value for the enthalpy of formation $\Delta_f H°_0$(GeC,g) = 627.2 ± 11 kJ mol^{-1}. Here we have weighted the results of each investigation proportional to the square root of the respective number of data points, $\sqrt{5}$ in the present investigation and for ref 10, $\sqrt{2}$ for the average of the 1810 and 1920 K values (635.8 kJ mol^{-1}), 1 for the 1860 K value (626.1 kJ mol^{-1}), and 1 for the 1765 K value (622.3 kJ mol^{-1}). The derived properties are $D_0° = 455.7 \pm 11)$ kJ mol^{-1}, $\Delta_f H°_{298.15} = 630.4 \pm 11$ kJ mol^{-1}, and $D°_{298.15} = 460.8 \pm 11$ kJ mol^{-1}.

The present thermodynamic evaluation of GeC(g) has been based on the value for $\Delta_f H°_{298.15}$(Ge,g) of 374.5 ± 2.1) kJ mol^{-1} from Hultgren et al.[29] This choice has been influenced by our previous use of the same value in our related investigations of Ge_2[21] and of gaseous germanium carbide clusters[5] and by our unpublished second-law average value of 374 ± 7) kJ mol^{-1} from two independent mass spectrometric measurements. Gurvich et al.[22] selected in the most recent assessment of this property, the value of 367.8 ± 1.0 kJ mol^{-1}, based on the work by Severin et al.[33] The work by Severin et al.[33] is based on Knudsen effusion studies and assumes the gas phase to consist of only Ge(g). It is known[34−36] that the equilibrium vapor of germanium contains germanium polymers up to Ge_7 in addition to Ge. We calculated from the relative intensities of Ge_2^+−Ge_7^+ [36] that at a temperature of 1700 K, these contribute as much as 6% of the partial pressure of Ge to the total pressure ($\sum_{i=1}^{7}(p_{Ge_i}/p_{Ge}) \approx 1.06$). This results in the overestimation of the partial pressure of Ge by as much as ≈16% in a Knudsen method experiment[33] and would add 1.4 kJ mol^{-1} to the value for the third law enthalpy of sublimation. This correction is outside the uncertainty limit of 1.0 kJ mol^{-1} chosen in refs 22 and 33.

The final report of the CODATA Task Group on Key Values for Thermodynamics gives $\Delta_f H°_{298.15}$(Ge,g) of 372 ± 3 kJ mol^{-1}.[37] CODATA doesn't yet consider the work on which Gurvich et al.[22] based their selected values. In our judgment, additional experimental work is called for the determination of the standard enthalpy of formation of Ge(g).

Using the standard heat of formation from Gurvich et al.[22] or from CODATA[37] would result in $\Delta_f H°_{298.15}$(GeC,g) = 623.7 ± 11 or 627.9 ± 11) kJ mol^{-1}, respectively.

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