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Atomization enthalpies and enthalpies of formation of the germanium clusters, Ge₅, Ge₆, Ge₇, and Ge₈ by Knudsen effusion mass spectrometry

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The high-temperature mass spectrometric method was employed to measure the equilibrium partial pressures of small germanium clusters above liquid germanium contained in a graphite Knudsen cell. These data were combined with new thermal functions, calculated from recent theoretical and spectroscopic molecular parameters, to evaluate the atomization enthalpies and enthalpies of formation of Ge₅–Ge₈. Mass spectrometric equilibrium data available in literature were also reevaluated. The following atomization enthalpies, $\Delta_a H_0^o(\text{Ge}_n, g)$ and enthalpies of formation $\Delta_f H_{298.15}^o(\text{Ge}_n, g)$, in kJ mol⁻¹, have been obtained: Ge₅, 1313±27 and 548±27, Ge₆, 1649±33 and 583±33, Ge₇, 2008±42 and 598±42, Ge₈, 2359±60 and 618±60. The atomization energies are compared with available theoretical values. © 2000 American Institute of Physics. [S0021-9606(00)00517-1]

INTRODUCTION

The bonding in germanium clusters is relevant in many fields of chemistry, for example, the stability of Ge₆₀ cage compounds,¹ growth of germanium nanoclusters,² and the etching of crystalline germanium surfaces.³ Furthermore, an understanding of how the cluster generation methods influence the size distribution of Ge clusters⁴ along with the stability of Ge_n ($n = 10$ –70) clusters⁵ may be obtained by a better understanding of the stability of small Ge_n clusters. Recent theoretical^{6–12} and experimental^{13–15} investigations of germanium clusters have focused on their geometries, electronic structures, spectroscopic constants, electron affinities, and binding energies.

Mass spectrometric work on germanium clusters began in the early 1950s.¹⁶ Drowart *et al.*¹⁷ reported the equilibrium partial pressure for Ge–Ge₆ at 1860 K, resulting from Knudsen effusion mass spectrometric experiments. Kant and Strauss¹⁸ obtained atomization enthalpies for Ge₂–Ge₇ from second- and third-law evaluations. Atomization energies from our laboratory have previously been reported for Ge₂,¹⁹ for Ge₃ and Ge₄,^{20,21} and for Ge₃–Ge₅.²²

In continuation of our studies of the thermodynamic stabilities of small homonuclear clusters^{21,23,24} employing the Knudsen effusion mass spectrometric method, we report here our results for the atomization energies and enthalpies of formation of the germanium clusters Ge₅–Ge₈. New thermal functions were calculated based on experimental and theoretical molecular parameters that have recently become available in the literature. For Ge₈ we have performed theoretical calculations of the molecular parameters needed. We also reevaluated the mass spectrometric literature equilibrium data for Ge₅–Ge₇ employing the new thermal functions

of the present work and correcting the reported partial pressures to be consistent with the assumptions used in the present study. All data have been combined into recommended assessed values for the atomization enthalpies, which are compared with recent theoretical results.

THERMAL FUNCTIONS

The harmonic-oscillator rigid-rotor approximation²⁵ was used in the evaluation of the Gibbs energy functions, $(G_T^o - H_0^o)/T$ (GEF₀), and enthalpy increments, $H_T^o - H_0^o$ (HCF₀), of Ge₅–Ge₈.

The vibrational frequencies for Ge₅ and Ge₆ have been taken from Lanza *et al.*⁹ for the ground state structures ¹A₁'(*D*_{3h}) (trigonal bipyramid) of Ge₅^{8,9} and ¹A₁(*C*_{2v}) (edge-capped trigonal bipyramid) of Ge₆,⁹ after multiplying them by a scaling factor of 0.9.²⁶ The same ground state structure as adopted for Ge₅ has been predicted for Si₅.²⁷

The bond lengths for the respective ground state structures have been taken from Dai and Balasubramanian for Ge₅ (Ref. 8) and from Lanza *et al.*⁹ for Ge₆.

For Ge₅ the transition energies, in cm⁻¹, from the multireference singles plus doubles configuration interaction (MRSDCI) calculations⁸ of 8300(³E''), 9000(¹E''), and 9400(³A₂') have been used for the *D*_{3h} structure. Eight other electronic transitions⁸ have also been considered, which correspond to the *C*_{4v} and *C*_{2v} point groups: *C*_{4v}: 8700(¹A₁); *C*_{2v}: 6500(³B₂), 6500(³B₁), 6500(³A₂), 8200(¹A₂), 7300(¹B₂), 7300(¹B₁), and 10 900(³A₁). For Ge₆ the experimental value 8106(³E'') from Burton *et al.*¹⁴ was used.

For the ground state structure of Ge₇, a slightly distorted pentagonal bipyramid (¹A₁), the vibrational frequencies and the bond lengths have been taken by Jackson *et al.*,⁷ and for the ground state structure of Ge₈ they have been calculated at the Hartree–Fock level of theory using a triple-zeta polarized and diffuse basis set, HF/6-31+G*. The thermal functions calculated for Ge₅–Ge₈ are given in Table I.

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TABLE I. The heat content function, $H_T^o - H_0^o$ (HCF₀) in kJ mol⁻¹ and the Gibbs energy functions, $(G_T^o - H_0^o)/T$ (GEF₀), in J/K⁻¹ mol⁻¹ of germanium polymers.

Species	Ge ₅		Ge ₆		Ge ₇		Ge ₈	
	HCF ₀	-GEF ₀						
298.15	24.54	314.4	30.14	361.8	35.62	377.2	40.24	406.5
1200	121.4	444.3	148.9	521.5	176.8	566.7	203.4	622.9
1400	143.7	460.0	175.5	540.7	208.4	589.5	239.9	649.2
1600	166.9	473.9	202.4	557.5	239.9	609.5	276.4	672.2
1800	191.2	486.3	229.4	572.5	271.5	627.2	313.0	692.6
2000	216.5	497.5	256.8	586.0	303.1	643.1	349.5	711.0
2200	242.8	508.0	284.5	598.2	334.7	657.6	386.1	727.7
2400	269.6	517.7	312.6	609.5	366.3	670.8	422.6	743.0

Our *ab initio* calculations on Ge₈ were carried out utilizing the GAUSSIAN 98 program package,²⁸ in order to obtain the molecular parameters and the vibrational frequencies of the Ge₈ ground state, which were used to calculate its thermal functions. The starting geometry of Ge₈ was assumed to be similar to the one calculated by Raghavachari and Rohlfiing²⁹ for the most stable ground state configuration of Si₈.

The optimized atomic separations, in Å, at the HF/6-31+G* level of theory, for the ¹A ground state of Ge₈, are: 2.694 (×4), 3.286, 3.214, 2.604 (×2), 2.603 (×2), 2.630, 2.631, 3.293, 2.365 (×2), 2.648, 2.649, 2.650 (×2). The harmonic vibrational frequencies, in cm⁻¹, scaled by a factor of 0.9,²⁶ are: 286, 281, 211, 202, 180, 173, 171, 165, 156, 152, 151, 147, 116, 106, 88, 76, 64, and 62.

EXPERIMENTAL PROCEDURE

A single focusing, 12 in. radius, magnetic deflection, 90° sector Nuclide Corporation Knudsen cell mass spectrometer was used in the present investigation. The specific instrument

and experimental procedures employed have been described elsewhere.³⁰ The measurements of the germanium clusters were performed in connection with the investigation of germanium carbides, series 1 (Refs. 31, 32) and series 2.³¹ Additional equilibrium data on Ge₅ have previously been obtained in our laboratory in connection with the investigation of palladium-germanium clusters above the system Pd-Ge (Refs. 33, 34) (series 3).

The ions were identified by their mass-to-charge ratios, ionization efficiency, and isotopic distribution. The electron energies, in eV, used are 14, 11, and 20 for series 1, series 2, and series 3, respectively. The ion intensity ratios, $I(\text{Ge}_n^+)/I(\text{Ge}^+)$, measured for the most abundant *m/e* ratios, are given in Table II for series 1 and 2. For series 3 the ion currents for Ge⁺ and Ge₅⁺ were taken from Kingcade.³³ The electron impact energy scale was calibrated with reference to the known first ionization potentials of Ge (7.88 V)³⁵ and/or Ag (7.57 V).³⁵ The average of the appearance potentials, in eV, are 8.0±0.6 and 7.8±0.6 for Ge₅ and Ge₆, respectively. These can be compared with the mass spectrometric values

TABLE II. Ion intensity ratios, $I(\text{Ge}_n^+)/I(\text{Ge}^+)$, measured in series 1 and 2.

T(K)	$I(\text{Ge}_5^+)/I(\text{Ge}^+)$	$I(\text{Ge}_6^+)/I(\text{Ge}^+)$	$I(\text{Ge}_7^+)/I(\text{Ge}^+)$	$I(\text{Ge}_8^+)/I(\text{Ge}^+)$	T(K)	$I(\text{Ge}_5^+)/I(\text{Ge}^+)$	$I(\text{Ge}_6^+)/I(\text{Ge}^+)$	$I(\text{Ge}_7^+)/I(\text{Ge}^+)$	$I(\text{Ge}_8^+)/I(\text{Ge}^+)$
	Series 1					Series 2			
1576	1.01E-3	6.40E-4			1351	3.26E-3	3.92E-3		
1598	6.46E-4	5.63E-4			1392	2.14E-3	3.06E-3		
1609	9.31E-4	5.14E-4			1429	2.08E-3	3.27E-3		
1638	1.07E-3	4.14E-4	6.90E-5		1477	1.87E-3	2.82E-3	2.05E-4	
1649	9.50E-4	6.26E-4	5.57E-5	7.95E-6	1518	2.06E-3	3.08E-3	2.32E-4	
1670	1.12E-3	6.67E-4	5.09E-5	8.49E-6	1566	1.48E-3	2.41E-3	1.63E-4	4.29E-6
1661	8.25E-4	6.98E-4	4.70E-5		1506	1.82E-3	2.90E-3	1.90E-4	
1680	7.75E-4	5.95E-4	5.66E-5		1547	1.70E-3	2.44E-3	1.56E-4	
1703	6.43E-4	5.03E-4	3.94E-5		1601	1.64E-3	2.21E-3	1.34E-4	2.78E-6
1668	8.52E-4	5.43E-4	4.17E-5		1638	1.31E-3	1.64E-3	8.55E-5	
1699	5.48E-4	4.47E-4	3.35E-5		1615	1.41E-3	1.83E-3	1.02E-4	
1719	4.94E-4	3.28E-4	3.31E-5		1427	1.90E-3	3.99E-3		
1744	6.14E-4	3.07E-4			1474	1.71E-3	2.95E-3		
					1547	1.70E-3	2.48E-3		
					1590	1.45E-3	1.85E-3		
					1628	1.29E-3	1.45E-3		
					1664	1.12E-3	8.23E-4		
					1535	8.01E-3	9.94E-4		
					1597	6.37E-4	7.19E-4		
					1649	4.33E-4			

TABLE III. Summary of the experimental enthalpy changes, in kJ mol^{-1} , for the dissociation reaction $\text{Ge}_n(\text{g}) = n \text{Ge}(\text{g})$ ($n=5$ and 6). The result from the reevaluated literature data and from the present investigation are given. The errors are standard deviations.

Reference	Temperature range (K)	No. of points	TM (K)	Second-law $\Delta_r H_{\text{TM}}^0$	Second-law $\Delta_r H_0^0$	Third-law $\Delta_r H_0^0$	Selected $\Delta_r H_0^0$
$\text{Ge}_5(\text{g}) = 5 \text{Ge}(\text{g})$							
Series 1	1576–1744	13	1656	1381.9 ± 54.9	1339.7 ± 54.9	1296.7 ± 5.5	1311.0
Series 2	1351–1664	20	1491	1372.8 ± 17.6	1330.3 ± 17.6	1304.6 ± 4.7	1313.2
Series 3	1680–1946	14	1803	1208.6 ± 41.8	1167.2 ± 44.8	1311.0 ± 8.1	1311.0^{a}
Ref. 18	1711–2004	6(15) ^b	1800	1384.9 ± 41.8	1344.0 ± 41.8	1306.8 ± 1.5	1319.2
Ref. 16	1300–1370	2				$1299.3 \pm 13.7^{\text{c}}$	1299.3
							$1312.5 \pm 27^{\text{d}}$
$\text{Ge}_6(\text{g}) = 6 \text{Ge}(\text{g})$							
Series 1	1576–1744	13	1656	1706.9 ± 57.4	1657.7 ± 57.4	1619.7 ± 5.8	1632.4
Series 2	1351–1664	19	1491	1731.3 ± 21.9	1683.0 ± 21.9	1637.1 ± 5.8	1652.4
Ref. 18	1663–1971	6(31) ^b	1800	1748.9 ± 54.4	1699.4 ± 54.4	1641.8 ± 1.5	1661.0
Ref. 16	1300–1370	2				$1637.7 \pm 15.9^{\text{c}}$	1637.7
							$1649.4 \pm 33^{\text{d}}$

^aSecond-law value was not considered due to the poor agreement with the corresponding third-law value.

^bNumber of data sets reevaluated; the actual number of data sets measured is given in parentheses (see text).

^cDeviation from the mean.

^dWeighed average; the errors are overall estimated errors (see text).

of 8.0 ± 0.5 for both, Ge_5 and Ge_6 ,¹⁸ and theoretical⁷ literature values of $7.15(\text{Ge}_5)$ and $7.43(\text{Ge}_6)$. The appearance potentials agree within the given error limits, except for the low theoretical value of Ge_5 .

The pressure calibration constant for germanium, k_{Ge} , was obtained for series 1 and 2 for each temperature from the measured ion intensities of Ge^+ by using the relation $p_i = k_i I_i T$, where $k_i = k/(\sigma n \gamma)_i$ is the pressure calibration constant, σ the ionization cross section, n the isotopic abundance, and γ the multiplier gain. The pressures used have been taken from Hultgren *et al.*³⁶ The resulting values for k_{Ge} , in $\text{bar A}^{-1} \text{K}^{-1}$, are 13.60 for series 1 and 6.14×10^{-2} for series 2.

The pressure calibration constant, k_{Ag} , in series 3 was obtained from the measured ion intensities of Ag^+ and Ag_2^+ (Ref. 33) and the known dissociation energy $D_0^0(\text{Ag}_2) = (158.0 \pm 3.4) \text{kJ mol}^{-1}$,³⁷ according to the procedure given by Cocke and Gingerich.³⁸ Fifteen data sets have been measured over a temperature range of 1210–1444 K using 20 V ionizing electrons. The experimentally determined³⁹ ratio of ionization cross section of silver dimer to that of monomer 2.0 was employed to obtain $k_{\text{Ag}} = (3.07 \pm 0.47) \times 10^2 \text{bar A}^{-1} \text{K}^{-1}$. The calibration constant for Ge, k_{Ge} , was derived employing the relation: $k_{\text{Ge}} = k_{\text{Ag}} \{(\sigma \gamma n)_{\text{Ag}} / (\sigma \gamma n)_{\text{Ge}}\}$. The ionization cross sections, in 10^{-16}cm^2 , of Ge (6.40) and Ag (4.50) were taken from Freund *et al.*⁴⁰ Also the experimental value, $\gamma_{\text{Ag}} / \gamma_{\text{Ge}}$, of 0.94 was used, yielding $k_{\text{Ge}} = 2.03 \times 10^{-2} \text{bar A}^{-1} \text{K}^{-1}$.

The pressure calibration constants for the germanium polymers, k_{Ge_i} , were derived from k_{Ge} employing the relation $k_{\text{Ge}_i} = k_{\text{Ge}} \{(\sigma \gamma n)_{\text{Ge}_i} / (\sigma \gamma n)_{\text{Ge}}\}$. The ratio of ionization cross sections of Ge_i to that of Ge was assumed to be 0.75 i and the multiplier gain of the polymers taken to be equal to that of the monomer, assuming cancellation of mass and molecular effects. The calibration constants, resulting for Ge_5 , Ge_6 , Ge_7 , and Ge_8 , in $\text{bar A}^{-1} \text{K}^{-1}$, are for series 1: 9.64,

9.15, 8.94, and 8.48, respectively; for series 2: 4.35×10^{-2} , 4.13×10^{-2} , 4.04×10^{-2} , and 3.83×10^{-2} , respectively; for series 3: 5.4×10^{-3} (for Ge_5).

RESULTS AND DISCUSSION

The enthalpy of the reaction,

$$\text{Ge}_n(\text{g}) = n \text{Ge}(\text{g}), \quad n = 5-8, \quad (1)$$

was evaluated according to the second-law method, based on a least-squares analysis of $\ln K_p$ vs. $1/T$ plots, and according to the third-law method, using the relation $\Delta_r H_0^0 = -RT \ln K_p - T\Delta[(G_T^0 - H_0^0)/T]$.

The results are presented in Table III for Ge_5 and Ge_6 , and in Table IV for Ge_7 and Ge_8 . Included in these tables are the temperature range of measurements and the number of data sets in each series of measurements. The second-law enthalpy of reaction at the mid temperature of measurements and at a reference temperature of 0 K, is also given along with the average of the third-law enthalpy for each series of measurement. For the germanium polymers, the thermal functions listed in Table I were used; those of $\text{Ge}(\text{g})$ were taken from Ref. 41. The selected reaction enthalpy for each series is the weighted average of the second-law value, a weight of 1, and the third-law value, a weight of 2, when both values are available. For Ge_7 the second-law value from the combined data of series 1 and 2 was used.

The mass spectrometric data for Ge_n^+ in Refs. 16, 17, and 18 have been reevaluated by (a) adopting the thermal functions used in the present work, (b) deriving the pressure calibration constant by taking the partial pressure of Ge adopted in the present work, and (c) by using a consistent set of data for ionization cross section and multiplier gains. The reevaluated results have been included in Tables III and IV.

In comparing the reevaluated literature data with the results of the present investigation, it must be noted that Kant and Strauss¹⁸ give only a few representative $I(\text{Ge}_n^+)/I(\text{Ge}^+)$

TABLE IV. Summary of the experimental enthalpy changes, in kJ mol^{-1} , for the dissociation reaction $\text{Ge}_n(g) = n \text{Ge}(g)$ ($n=7$ and 8). The results from the reevaluated literature data and from the present investigation are given. The errors are standard deviations.

Reference	Temperature Range (K)	No. of points	TM (K)	Second-law $\Delta_r H_{\text{TM}}^{\circ}$	Second-law $\Delta_r H_0^{\circ}$	Third-law $\Delta_r H_0^{\circ}$	Selected $\Delta_r H_0^{\circ}$
$\text{Ge}_7(g) = 7 \text{Ge}(g)$							
Series 1	1638–1719	9	1676	2221.9 ± 90.2	2168.5 ± 90.2	2020.5 ± 4.6	2020.5
Series 2	1477–1615	8	1556	2050.7 ± 56.7	1998.0 ± 56.7	2022.2 ± 5.5	2022.2
Series 1 + 2	1477–1719	17	1617	2091.2 ± 26.3	2038.1 ± 26.3	2021.3 ± 4.9	2026.9
Ref. 18	1586–1927	5(10) ^a	1800	2058.5 ± 62.8	2004.3 ± 62.8	1964.5 ± 0.8	1977.8
Ref. 16	1300–1370	2				1993.5 ± 7.2^b	1993.5
							2008 ± 42^c
$\text{Ge}_8(g) = 8 \text{Ge}(g)$							
Series 1	1649–1670	2	2371 ± 11^b	2371
Series 2	1566–1601	2	2346 ± 4^b	2346
							2359 ± 60^c

^aNumber of data sets reevaluated; the actual number of data sets measured is given in parentheses (see text).

^bDeviation from the mean.

^cWeighed average; the errors are overall estimated errors (see text).

ratios on which our third-law reevaluation is based. Our reevaluation of their second-law value is based on the result given in their article at the mid temperature of 1800 K, which is corrected to 0 K reference temperature, by using our enthalpy increments from Table I. The actual number of measurements for each Ge_n is given by Kant and Strauss as 15 for Ge_5 , 31 for Ge_6 , and 10 for Ge_7 . This may explain the very small standard deviations for the reevaluated third-law $\Delta_r H_0^{\circ}$ values from Ref. 18. The errors for the second-law values given in Tables III and IV are those estimated by Kant and Strauss. The results by Honig¹⁶ show a large deviation from the mean but the mean value is just slightly lower than the recommended value. This may be taken as an indication that the vaporization coefficient of liquid germanium is close to unity. The single set of data by Drowart *et al.*¹⁷ yields, for Ge_5 and Ge_6 , an atomization energy that is about 30 and 38 kJ mol^{-1} , respectively, lower than the average from the other investigations. It has therefore not been included in our respective weighted average, and is not shown in Table III.

Fragmentation does not appear to be a problem. It would be expected to be largest for the data from Refs. 16 and 18, for which the largest electron impact energies, 45 and 20 or 70 eV, respectively, were used to produce the Ge_n^+ ions. Already Kant and Strauss¹⁸ have noted that the $I(\text{Ge}_n^+)/I(\text{Ge}^+)$ ratios are independent of the electron energy, between 20 and 70 eV, used.

For Ge_7 we have also combined all data, series 1 plus series 2, for an evaluation, of a reliable second-law value, because of the few data points of each series and the short temperature range covered. The individual results for each series are shown for comparison. It can be noted that the selected value from Ref. 18 is about 50 kJ mol^{-1} lower than our selected value, and their second-law value is closer to ours.

For Ge_8 we obtained the first mass spectrometric value of its $\Delta_a H_0^{\circ}$. The large overall error is mainly due to the few data and the scatter between them.

The recommended value for the atomization energy of Ge_5 , Ge_6 , Ge_7 , and Ge_8 , which is the enthalpy of reaction 1, was obtained as the weighted average of the respective se-

lected $\Delta_r H_0^{\circ}$ values, resulting from the various investigations, given in Tables III and IV. The weight for each series or each literature value, respectively, was taken as the square root of number of data points. In the case of Ref. 18, the number of points was taken as those given in parenthesis in Tables III and IV of the original article. The resulting $\Delta_a H_0^{\circ}$ values, in kJ mol^{-1} , are: 1312.5 ± 27 for Ge_5 , 1649.4 ± 33 for Ge_6 , 2008 ± 42 for Ge_7 , and 2359 ± 60 for Ge_8 . Here the uncertainties are overall uncertainties, calculated from estimated uncertainties according to the procedure given by Schmude *et al.*⁴² The corresponding values of $\Delta_a H_{298.15}^{\circ}$, $\Delta_f H_0^{\circ}$, and $\Delta_f H_{298.15}^{\circ}$ for Ge_5 , Ge_6 , Ge_7 , and Ge_8 have been derived from these $\Delta_r H_0^{\circ}$ values, using $\Delta_f H_0^{\circ}(\text{Ge}, g) = (371.7 \pm 2.1) \text{kJ mol}^{-1}$,³⁶ or $\Delta_f H_{298.15}^{\circ}(\text{Ge}, g) = (374.5 \pm 2.1) \text{kJ mol}^{-1}$,³⁶ respectively, and the $H_{298.15}^{\circ} - H_0^{\circ}$ values from Table I. For the calculation of enthalpies of formation the relation $\Delta_f H_T^{\circ}(\text{Ge}_n) = n \Delta_f H_T^{\circ}(\text{Ge}) - \Delta_a H_T^{\circ}(\text{Ge}_n)$, where T is 0 or 298.15 K, was used.

The thermodynamic properties for Ge_5 – Ge_8 clusters have been summarized in Table V.

From the $\Delta_a H_0^{\circ}$ values, the fragmentation enthalpies or incremental dissociation energies, $\Delta_a H_0^{\circ}(\text{Ge}_n) - \Delta_a H_0^{\circ}(\text{Ge}_{n-1})$, can be derived. They are, in kJ mol^{-1} or eV, 343 or 3.56, 337 or 3.49, 359 or 3.72, and 351 or 3.64, for Ge_5 , Ge_6 , Ge_7 , and Ge_8 , respectively. The value for Ge_5 has been obtained from $\Delta_a H_0^{\circ}(\text{Ge}_4)$ of $(969.4 \pm 24) \text{kJ mol}^{-1}$ or 10.05 eV.²¹

The enthalpies of formation of Ge_5 , Ge_6 , Ge_7 , and Ge_8 , listed in Table V, have been obtained from the present atomization energies and the enthalpy of sublimation from

TABLE V. Thermodynamic properties for the germanium clusters, Ge_5 – Ge_8 . All values are in kJ mol^{-1} .

Cluster	$\Delta_a H_0^{\circ}$	$\Delta_a H_{298.15}^{\circ}$	$\Delta_f H_0^{\circ}$	$\Delta_f H_{298.15}^{\circ}$
Ge_5	1313 ± 27	1325 ± 27	546 ± 27	548 ± 27
Ge_6	1649 ± 33	1664 ± 33	581 ± 33	583 ± 33
Ge_7	2008 ± 42	2024 ± 42	594 ± 42	598 ± 42
Ge_8	2359 ± 60	2378 ± 60	615 ± 60	618 ± 60

TABLE VI. Comparison of experimental atomization energies, in eV, with recent theoretical values for Ge₅–Ge₈.

Cluster	Experiment			Theoretical		
	This invest.	G2 ^a	G2(MP2) ^a	B3LYP ^a	NLSD/BLYP ^b	Tight-Binding ^c
Ge ₅	13.61 ± 0.28	13.59	13.38	12.53	12.39	14.25
Ge ₆	17.09 ± 0.34				16.44	18.30
Ge ₇	20.81 ± 0.44				19.76	22.33
Ge ₈	24.45 ± 0.62					25.36

^aReference 10.^bReference 7.^cReference 12.

Hultgren *et al.*³⁶ With the standard enthalpy of formation for atomic germanium, $\Delta_f H_{298.15}^o(\text{Ge}, g) = (372.0 \pm 3) \text{ kJ mol}^{-1}$, from CODATA,⁴³ the standard enthalpies of formation, $\Delta_f H_{298.15}^o(\text{Ge}_n, g)$, for the germanium clusters derived from the corresponding atomization enthalpies, in kJ mol^{-1} , become 535.0 ± 27 for Ge₅, 568.4 ± 33 for Ge₆, 580 ± 42 for Ge₇, and 598 ± 60 for Ge₈. With $\Delta_f H_{298.15}^o(\text{Ge}, g) = (367.8 \pm 1) \text{ kJ mol}^{-1}$, from Gurvich *et al.*,⁴¹ the $\Delta_f H_{298.15}^o(\text{Ge}_n, g)$ values, in kJ mol^{-1} , result in 514.0 ± 27 for Ge₅, 543.2 ± 33 for Ge₆, 551 ± 42 for Ge₇, and 564 ± 60 . Clearly, the choice of the enthalpy of formation of atomic germanium has a significant effect on the enthalpy of formation of the gaseous germanium clusters.

The atomization energy derived from series 3 for Ge₅ has been based on data measured over a liquid germanium–palladium alloy using the well-known dissociation energy of Ag₂.³⁷ The selected third-law atomization enthalpy, Table III, obtained from these data is practically the same as the selected value obtained from all data.

The enthalpy of formation for atomic germanium selected by Hultgren *et al.*³⁶ is supported by our second-law average $\Delta_f H_{298.15}^o(\text{Ge}, g)$ of $(374 \pm 7) \text{ kJ mol}^{-1}$ obtained from the $I(\text{Ge}^+)$ data for series 1 and 2.

It is also interesting to calculate the binding energies, or atomization enthalpies, $\Delta_a H_0^o$, of the germanium clusters anions for the reaction $\text{Ge}_n^-(g) = (n-1)\text{Ge}(g) + \text{Ge}^-(g)$, using the experimental values of their electron affinities (EA). The results, in eV, are 10.8, 14.9, 17.9, 21.4, and 25.6 for Ge₄⁻, Ge₅⁻, Ge₆⁻, Ge₇⁻, and Ge₈⁻, respectively. The relation used is $\Delta_a H_0^o(\text{Ge}_n^-) = \Delta_a H_0^o(\text{Ge}_n) - \text{EA}(\text{Ge}) + \text{EA}(\text{Ge}_n)$. The experimental electron affinities were taken from Burton *et al.*¹⁴ for Ge₄–Ge₈, and from Miller *et al.*⁴⁴ for the atomic Ge. The corresponding fragmentation enthalpies or incremental dissociation energies, $\Delta_a H_0^o(\text{Ge}_n^-) - \Delta_a H_0^o(\text{Ge}_{n-1}^-)$, in eV, are 4.1(Ge₅⁻), 3.0(Ge₆⁻), 3.5(Ge₇⁻), and 4.2(Ge₈⁻). The trend in these values mainly reflects the trend in the corresponding EA values, e.g., large values for Ge₅ and Ge₈.¹⁴

COMPARISON OF EXPERIMENTAL AND THEORETICAL ATOMIZATION ENTHALPIES

In recent years theoretical methods have advanced to become chemically accurate in predicting binding energies for small clusters. This has been illustrated by Raghavachari and Curtiss⁴⁵ who compared the atomization energies (bind-

ing energies) obtained by the Gaussian-2 (G2) theory with the corresponding experimental values reported from our laboratory for small carbon and silicon clusters. Recently the G2 theory has been extended to elements containing third-row atoms Ga–Kr (Ref. 46) and Deutsch *et al.*¹⁰ have applied it to Ge₂ through Ge₅.

In Table VI we compare their results with recent predictions by other theoretical methods with the experimental atomization energies of Ge₅–Ge₈ obtained in the present investigation.

As can be seen from Table VI, for Ge₅ there is excellent agreement between the present experimental results and the predictions from the G2 theory.¹⁰ The G2 (MP2) (Ref. 10) prediction, Gaussian-2 method using the second-order Møller–Plesset perturbation theory, also agrees within the error limits of the experimental value, whereas the density functional method, using the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP), predicts a value of 12.53 eV, 92% of the experimental value. The nonlocal spin density theory employing the B3LYP functional (NLSD/BLYP) results of Jackson *et al.*⁷ account for about 95% of the binding energies for Ge₅–Ge₇. Menon¹² has used a minimal-parameter tight-binding theory to predict partially scaled values for all the clusters studied in the present investigation. His values are approximately 1 eV larger than ours.

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