

- (29) S. Yanagisawa, M. Tashiro, and S. Anzai, *J. Inorg. Nucl. Chem.*, **31**, 943 (1969).
- (30) J. M. Hastings, N. Elliott, and L. M. Corliss, *Phys. Rev.*, **115**, 13 (1959).
- (31) P. Cherin and P. Unger, *Acta Crystallogr., Sect. B*, **23**, 670 (1967).
- (32) R. J. Gillespie, W. Luk, E. Maharajh, and D. R. Slim, *Inorg. Chem.*, **16**, 892 (1977).
- (33) J. D. Corbett, *Inorg. Nucl. Chem. Lett.*, **5**, 81 (1969).
- (34) R. C. Burns, R. J. Gillespie, and M. J. McGlinchey, manuscript in preparation.
- (35) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972.
- (36) F. B. Clifford and L. S. Bartell, *Inorg. Chem.*, **9**, 805 (1970).
- (37) S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, **43**, 1693 (1970).
- (38) P. Boldrini, I. D. Brown, R. J. Gillespie, P. R. Ireland, W. Luk, D. R. Slim, and J. E. Vekris, *Inorg. Chem.*, **15**, 765 (1976).
- (39) B. Post, R. S. Schwatz, and I. Faukuchen, *Acta Crystallogr.*, **5**, 372 (1952).
- (40) M. Schmidt and W. Seibert in "Comprehensive Inorganic Chemistry", Pergamon Press, Oxford, 1973, Chapter 23.
- (41) A. Caron and J. Donahue, *Acta Crystallogr.*, **18**, 562 (1965).
- (42) O. Foss and V. Janickis, *J. Chem. Soc., Chem. Commun.*, 834 (1977), and references therein.
- (43) C. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).
- (44) R. K. Mullen, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, **10**, 1749 (1971); *Chem. Commun.*, 1438 (1969).
- (45) S. A. A. Zaidi, Z. A. Siddiqui, and N. A. Ansari, *Acta Chim. Acad. Sci. Hung.*, **97**, 207 (1978).
- (46) R. Kapoor, Ph.D. Thesis, McMaster University, 1968.
- (47) R. J. Gillespie, D. R. Slim, and J. D. Tyrer, *J. Chem. Soc., Chem. Commun.*, 253 (1977).
- (48) R. De Vries and F. C. Mijlhoff, *Acta Crystallogr., Sect. B*, **25**, 1696 (1969).

Contribution from the Department of Chemistry,  
Texas A&M University, College Station, Texas 77843

## Stability and Thermodynamics of Ligand-Free Germanium-Gold Clusters<sup>1</sup>

J. E. KINGCADE, JR., U. V. CHOUDARY, and K. A. GINGERICH\*

Received March 5, 1979

The equilibria involving gaseous species above the condensed Au-Ge-Cu system have been investigated by the high-temperature mass spectrometric technique. The molecules Au<sub>2</sub>, AuCu, AuGe, Au<sub>2</sub>Ge, AuGe<sub>2</sub>, Au<sub>2</sub>Ge<sub>2</sub>, AuGe<sub>3</sub>, AuGe<sub>4</sub>, Ge<sub>2</sub>, Ge<sub>3</sub>, and Ge<sub>4</sub> were shown to exist in the vapor phase above the liquid solution. Second- and third-law enthalpy changes have been determined from the experimental data for the following gaseous reactions: AuCu = Au + Cu, AuCu + Au = Au<sub>2</sub> + Cu, AuGe = Ge + Au, AuGe + Au = Ge + Au<sub>2</sub>, AuGe + Cu = AuCu + Ge, Au<sub>2</sub>Ge = Ge + 2Au, Au<sub>2</sub>Ge + Ge = 2AuGe, AuGe<sub>2</sub> = 2Ge + Au, AuGe<sub>2</sub> + Au = 2AuGe, Ge<sub>2</sub> = 2Ge, Ge<sub>2</sub> + Au = Ge + AuGe. In addition, third-law enthalpy changes were evaluated for the following gaseous reactions: Au<sub>2</sub>Ge<sub>2</sub> = 2AuGe, AuGe<sub>3</sub> + 2Au = 3AuGe, AuGe<sub>4</sub> + 3Au = 4AuGe, Ge<sub>3</sub> + Ge = 2Ge<sub>2</sub>, Ge<sub>4</sub> = 2Ge. The values of these reaction enthalpies have then been combined with ancillary literature data to give the dissociation energies,  $D^\circ_{298}$ , of the diatomic molecules, and the atomization energies,  $\Delta H^\circ_{a,298}$ , of the various polyatomic molecules assuming different molecular configurations. A preferred molecular structure along with the resulting atomization energy,  $\Delta H^\circ_{a,298}$  (kJ mol<sup>-1</sup>), and the corresponding standard heat of formation,  $\Delta H^\circ_{f,298}$  (kJ mol<sup>-1</sup>), respectively, are presented for the following previously unreported gaseous molecules: Au<sub>2</sub>Ge (bent, 538 ± 12, 573 ± 12), AuGe<sub>2</sub> (bent, 535 ± 10, 581 ± 10), Au<sub>2</sub>Ge<sub>2</sub> (linear, 934 ± 14, 551 ± 14), AuGe<sub>3</sub> (linear, 903 ± 20, 582 ± 20), AuGe<sub>4</sub> (trigonal bipyramid, 1307 ± 30, 559 ± 30). The previously known molecules AuCu, Ge<sub>2</sub>, Ge<sub>3</sub>, and Ge<sub>4</sub> have also been evaluated in this investigation, yielding the atomization energies of 227 ± 5, 260 ± 10, 637 ± 20, and 989 ± 22 kJ mol<sup>-1</sup>, respectively. These values are within the error limits of the reported literature values. Finally, a thorough evaluation of the dissociation energy (referenced to 298 K) 272.6 ± 5.0 kJ mol<sup>-1</sup> and the standard heat of formation 470.0 ± 5.0 kJ mol<sup>-1</sup> has been performed on the molecule AuGe(g).

### Introduction

Investigation into the physical and chemical properties of small atomic and molecular aggregates, particularly metal clusters, has been quite intensive over the last 2 decades. This interest stems from recognizing the key role these small aggregates play in such areas as homogeneous nucleation and crystal growth.<sup>2-5</sup> Experimental knowledge of binding energies and structures of microscopic clusters may aid the theoretician in the estimation of configurational entropies.<sup>6</sup> Also, small atomic metal aggregates are important in photographic systems. These dispersed metal clusters<sup>7-10</sup> are found to be better or worse catalysts because of size effects and geometrical arrangement of atoms. Thus an estimation of cluster geometry may assist in producing a theory that may predict the catalytic effect beforehand.

We have previously reported<sup>11</sup> on the stability of the molecules AuSn, Au<sub>2</sub>Sn, AuSn<sub>2</sub>, Au<sub>2</sub>Sn<sub>2</sub>, and AuSn<sub>3</sub> derived from Knudsen cell mass spectrometric measurements. Therefore, in keeping with this current interest in gaseous heteronuclear polyatomic molecules of gold, we have examined the gaseous molecules above the gold-germanium system. Since germanium and tin are known to form similar gaseous homonuclear polyatomic molecules, similar gaseous intermetallic molecules could be expected for the Ge-Au system, as for the Au-Sn system.<sup>11</sup> The Au-Ge system was also

expected to offer the optimum experimental conditions for observing even higher polyatomic molecules, because of the similar vaporization enthalpies and equilibrium pressures of the component elements gold and germanium. Concomitant to this objective was the independent redetermination of the atomization energies of Ge<sub>2</sub>, Ge<sub>3</sub>, and Ge<sub>4</sub>. Also, an improved evaluation of the gaseous diatomic molecule AuCu was performed, due to the incorporation of a small amount of elemental copper within the condensed mixture.

A preliminary account of the atomization energies of the four- and five-atom germanium-gold molecules has been given elsewhere.<sup>12</sup>

### Experimental Section

The mass spectrometer employed for this investigation is a single-focusing, 12-in. radius, magnetic deflection, 90° sector, Knudsen cell, high-temperature instrument. The spectrometer<sup>13</sup> and the experimental procedure<sup>13,14</sup> have been discussed elsewhere.

The sample used in the present investigation was 0.49-0.49-0.02 M Au-Ge-Cu alloy. Commercially purchased 99.9+% germanium and gold from the National Bureau of Standards. The sample was contained in a graphite cell that was inserted in a tantalum Knudsen cell, both cells having centric, close to knife-edge orifices of 1 mm diameter.

The instrument was standardized at an emission current of 1 mA, which was sustained throughout the experiment. The ions were

Table I. Experimental and Estimated Parameters Used in the Evaluation of Calibration Constants for the System Ge–Au–Cu<sup>a</sup>

ion	ionization cross sections $\sigma$ , Å <sup>2</sup>	rel multiplier gain $\gamma_i/\gamma_{Au}$	intens correctn factor $E_i$	calibration const $k_i$ , atm A <sup>-1</sup> K <sup>-1</sup>
Au <sup>+</sup>	5.85	1.00	1.17	0.367 <sup>b</sup>
Au <sub>2</sub> <sup>+</sup>	8.78	1.00	1.17 <sup>c</sup>	0.246 <sup>b</sup>
Cu <sup>+</sup>	3.80	1.77	1.05	0.414
Ge <sup>+</sup>	5.71	1.37	1.06	0.679
Ge <sub>2</sub> <sup>+</sup>	8.56	1.37	1.02	0.671
Ge <sub>3</sub> <sup>+</sup>	12.85	1.37	1.02 <sup>c</sup>	0.542
Ge <sub>4</sub> <sup>+</sup>	17.13	1.37	1.02 <sup>c</sup>	0.508
AuCu <sup>+</sup>	7.24	1.38	1.07	0.284
AuGe <sup>+</sup>	8.67	1.19	1.05	0.510
Au <sub>2</sub> Ge <sup>+</sup>	13.06	1.12	1.05 <sup>c</sup>	0.360
AuGe <sub>2</sub> <sup>+</sup>	12.95	1.25	1.05 <sup>c</sup>	0.500
Au <sub>2</sub> Ge <sub>2</sub> <sup>+</sup>	17.34	1.19	1.05 <sup>c</sup>	0.392
AuGe <sub>3</sub> <sup>+</sup>	17.23	1.28	1.05 <sup>c</sup>	0.446
AuGe <sub>4</sub> <sup>+</sup>	21.52	1.28	1.05 <sup>c</sup>	0.446

<sup>a</sup> See text for details. <sup>b</sup>  $k_i$  constant giving best third-law value for the gaseous reaction  $Au_2 = 2Au$  of  $D_{298}^\circ = 223.4$  kJ mol<sup>-1</sup>.  
<sup>c</sup> Estimated values.

investigated by employing an ionizing electron energy of 20 eV, 4.5-kV ion acceleration voltage, and 1.9 kV at the entrance shield of the electron multiplier.

Any errors due to ion trapping are estimated by us to be less than 7% of measured ion currents and included in the first error limits. The temperature of the cell was measured with a calibrated Leeds and Northrup optical pyrometer by sighting on a threaded black-body cavity at the base of the tantalum cell and the extent of the temperature range in this investigation was 1400–2060 K.

The ionic species Au<sup>+</sup>, Au<sub>2</sub><sup>+</sup>, Ge<sup>+</sup>, Ge<sub>2</sub><sup>+</sup>, Ge<sub>3</sub><sup>+</sup>, Ge<sub>4</sub><sup>+</sup>, AuGe<sup>+</sup>, Au<sub>2</sub>Ge<sup>+</sup>, AuGe<sub>2</sub><sup>+</sup>, Au<sub>2</sub>Ge<sub>2</sub><sup>+</sup>, AuGe<sub>3</sub><sup>+</sup>, AuGe<sub>4</sub><sup>+</sup>, and AuCu<sup>+</sup> were identified by their  $m/z$  ratio, shutterability, isotopic distribution, and ionization efficiency curves (where possible). Carbon-containing species of germanium were also observed at the highest temperatures. In addition, the gaseous ion species Cu<sup>+</sup>, CuGe<sup>+</sup>, and CuGe<sub>2</sub><sup>+</sup><sup>16</sup> were identified.

## Results and Discussion

**A. Calibration of Partial Pressures from Intensity Data.** The measured ion intensities of the species relevant to the evaluation of the enthalpy changes for the various reactions considered can be obtained as supplementary material.

Absolute pressures at any given temperature  $T$  (K) for a particular species (i) were derived from these intensity data according to the relation

$$P_i = k_j [G_j N_j E_i / G_i (\gamma_i / \gamma_j) N_i E_j] I_i^+ T$$

where  $P$  is the pressure in atm,  $k_j$  is the reference calibration constant (for reference species  $j$ ) in atm A<sup>-1</sup> K<sup>-1</sup>, the ion intensities are represented by  $I_i^+$  expressed in A, and  $T$  is the temperature in K. The other parameters  $G$ ,  $\gamma$ ,  $N$ , and  $E$  are the ionization cross section, multiplier gain, isotopic abundance, and intensity correction factor, respectively, and the values are all listed in Table I.

A reference calibration constant  $k_j(Au) = 0.367$  atm A<sup>-1</sup> K<sup>-1</sup> was obtained from the equilibrium dissociation of  $Au_2(g) = 2Au(g)$ <sup>14</sup> where the enthalpy change of this reaction was taken as  $\Delta H^\circ_0 = 221.3$  kJ mol<sup>-1</sup>, from published data by Kordis et al.<sup>17</sup>

Relative multiplier gains ( $\gamma_i$ ) for the atomic ions were taken from an earlier investigation<sup>18</sup> using a similar mass spectrometer. Values for the relative multiplier gains of the various homonuclear molecules were assumed equal to that of the atoms. The  $\gamma_i$  values for mixed species were obtained by taking the arithmetic means of the  $\gamma_i$  value of the composite atoms. The relative maximum ionization cross sections for singly ionized atomic species were taken from Mann.<sup>19</sup> Ionization cross sections of diatomic and polyatomic molecules were

estimated as 0.75 times that of the sum of the cross sections of the composite elements.<sup>15</sup> Experimental ionization efficiency curves (where applicable) provided an empirical correction factor  $I_i^+(\text{max})/I_i^+(\text{meas}) = E_i$ . This factor was employed to bring the measured intensities at 20 eV in accord with the maximum intensities for which the tabulated cross sections by Mann apply. Where no ionization efficiency curves were available, intensity correction factors were estimated from related measured molecules. The various measured and estimated instrument parameters are listed in Table I.

**B. Calculation of Thermal Functions.** The thermodynamic functions of molecules in the gas phase can be calculated by using available computer programs employing standard statistical thermodynamic relations.<sup>20</sup> Vibrational frequencies for the various molecules were evaluated by using a valence force field calculation, utilizing a modification of the Schachtschneider computer program.<sup>21</sup> This program employs the Wilson FG matrix method.<sup>22</sup> The free-energy functions,  $-(G^\circ_T - G^\circ_0)/T$ , and the enthalpy functions,  $H^\circ_T - H^\circ_0$ , were calculated by using the rigid rotator harmonic oscillator approximation.

Ancillary thermal functions for the gaseous species Au, Ge, and Cu were taken from the compilation of Hultgren et al.,<sup>23</sup> those for Au<sub>2</sub> were from Kordis et al.,<sup>17</sup> and those for Ge<sub>2</sub>, Ge<sub>3</sub>, and Ge<sub>4</sub> were from Drowart et al.<sup>24</sup>

**AuCu and AuGe.** The thermal functions for gaseous AuCu were calculated by using the same molecular parameters ( $r_e = 2.51$  Å,  $\omega_e = 250$  cm<sup>-1</sup> (estimated), and an assumed <sup>1</sup>Σ ground state) as Ackerman et al.,<sup>25</sup> those of AuGe were calculated by using the experimental vibrational frequency  $\omega_e = 249.7$  cm<sup>-1</sup> and electronic states X<sub>1</sub> (<sup>2</sup>π<sub>1/2</sub>, 0 cm<sup>-1</sup>), X<sub>2</sub> (<sup>2</sup>π<sub>3/4</sub>, 1554 cm<sup>-1</sup>), and A (<sup>2</sup>Σ<sup>+</sup>, 13 743 cm<sup>-1</sup>).<sup>26,27</sup> The equilibrium separation  $r_e = 2.38$  Å was calculated from the vibrational frequency and the force constant 2.03 mdyn/Å given by Barrow et al.<sup>27</sup>

Houdart and Schamps<sup>26</sup> attempted to demonstrate that the <sup>2</sup>π ground state for the molecule AuGe results from a (5d<sup>10</sup><sub>Au</sub>σ<sup>2</sup><sub>Ge</sub>π<sub>Ge</sub>) configuration and corresponds to the ionic structure Au<sup>+</sup>Ge<sup>-</sup>. They postulated that the molecular orbitals corresponding to the closed-shell 5d(Au) atomic orbital remain closed-shell orbitals in the molecule. This assumption had already been suggested for the molecules CuO and AgO by Cheetham and Barrow.<sup>28</sup> These two molecules can be compared with AuGe since the p<sup>2</sup> occupation in Ge is substituted by p<sup>2</sup> holes in O and since Cu, Ag, and Au all have similar valence electron structures. An ionic analogy may then also be used on the remaining polyatomic Au–Ge molecules. This ionic univalence of Au will be assumed as the preferred structure of the higher polyatomic molecules, discussed below, but at times other valence states of gold will be considered for comparison.

**Au<sub>2</sub>Ge and AuGe<sub>2</sub>.** Spectroscopically determined molecular parameters for AuGe<sub>2</sub> and Au<sub>2</sub>Ge would be needed for an accurate determination of their thermal functions. Because of the lack of such information, we have considered various structures in the context with related available information. A symmetric structure for the molecule Au<sub>2</sub>Ge and an asymmetric structure for AuGe<sub>2</sub> were chosen. One reason for choosing these structures is the assumed preferred monovalent state of Au.

The symmetric structure for the molecule Au<sub>2</sub>Ge is also indicated from the analogy to the nonlinear GeH<sub>2</sub>.<sup>29</sup> It is known that hydrogen and gold have similar electronegativities ( $X_H = 2.1$  and  $X_{Au} = 2.2$ <sup>30</sup>) if adjusted to correspond to the same valence state. The bond angle for the molecule GeH<sub>2</sub> has been estimated by Smith and Guillory<sup>29</sup> as slightly wider angles than for SiH<sub>2</sub> and CH<sub>2</sub>, which are 92<sup>31</sup> and 104<sup>32</sup>, respectively. Also, a bending force constant equal to ap-

Table II. Calculated Vibrational Frequencies (in  $\text{cm}^{-1}$ ) of the Gaseous Polyatomic Germanium-Gold Molecules

molecule	$\omega_1$	$\omega_2$	$\omega_3$
Au <sub>2</sub> Ge (L)	335	120 dd	132
(B)	285	68	233
AuGe <sub>2</sub> (L)	409	145 dd	183
(B)	376	98	254

molecule	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$	$\omega_6$
Au <sub>2</sub> Ge <sub>2</sub> (L)	434	112	255	306 dd	87 dd	
(SP)	271	111	263	270	255	58
(tetra)	423	174	251	288	216	168
AuGe <sub>3</sub> (L)	464	146	316	312 dd	107 dd	
(tetra)	476	206	340	341	241	206

molecule	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$	$\omega_6$	$\omega_7$	$\omega_8$	$\omega_9$
AuGe <sub>4</sub> (L)	487	258	391	123	288 dd	140 dd	54 dd		
(TB)	550	270	412	236	410	271	382	133	51
(tetra)	415	127	355	102	413	218	126	93	92

Table III. Free-Energy Functions,  $-(G^\circ_T - H^\circ_0)/T$ , in  $\text{J K}^{-1} \text{mol}^{-1}$ , and Heat Content Functions,  $(H^\circ_T - H^\circ_0)$ , in  $\text{kJ mol}^{-1}$ , for the Gaseous Molecules AuCu, AuGe, Au<sub>2</sub>Ge, and AuGe<sub>2</sub>

molecule (struct)	function	temp, K						
		298	1200	1400	1600	1800	2000	2200
AuCu	FEF	228.6	277.4	283.0	287.9	292.2	296.1	299.6
	HCF	9.954	43.47	50.96	58.41	65.90	73.39	80.83
AuGe	FEF	234.7	284.7	290.7	295.8	300.4	304.5	308.2
	HCF	9.958	45.98	54.06	62.09	70.04	77.95	85.77
Au <sub>2</sub> Ge (linear)	FEF	277.1	354.4	363.6	371.5	378.6	384.9	390.7
	HCF	15.10	70.79	83.22	95.69	108.2	120.6	133.0
Au <sub>2</sub> Ge (bent)	FEF	303.5	376.7	385.3	392.8	399.4	405.3	410.7
	HCF	14.50	66.48	78.12	89.75	101.4	113.0	124.6
AuGe <sub>2</sub> (linear)	FEF	269.8	345.1	354.2	362.0	369.0	375.3	381.6
	HCF	14.43	69.83	82.26	94.72	107.2	119.6	132.0
AuGe <sub>2</sub> (bent)	FEF	296.8	368.5	377.0	384.4	390.9	396.8	402.2
	HCF	13.99	65.73	77.36	88.95	100.6	112.2	123.8

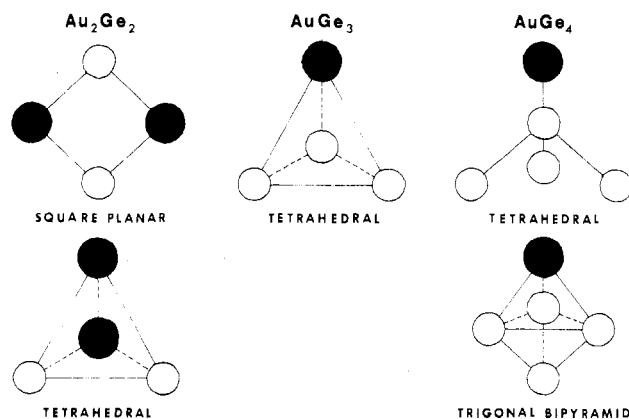
proximately one-tenth of the arithmetic mean of the stretching force constants was indicated in the above coordinate analysis of GeH<sub>2</sub>.

Matrix isolation studies of germanium dichloride<sup>33,34</sup> indicated that this molecule is also bent. The investigators were unable to determine accurately the bond angle of GeCl<sub>2</sub> but estimated an angle of approximately  $100 \pm 10^\circ$ .

Assimilating the above experimental data, we expect a bent structure for Au<sub>2</sub>Ge(g) and an angle of  $110^\circ$  has been assumed (this angle is estimated equal to the upper limit of the reported angle of the molecule GeCl<sub>2</sub>). An uncertainty in the molecular angle of  $10^\circ$  produces only an uncertainty in the free-energy function of approximately 0.5%.

A Ge-Au bond distance of 2.38 Å, with a stretching force constant of 2.03 mdyne/Å, was chosen the same as for the diatomic molecule GeAu. A bending force constant is estimated as one-tenth of the arithmetic mean of the stretching force constants associated with the angle bend, which was calculated as 0.20 mdyne/Å. The electronic contribution to the free-energy function was assumed to be  $11.50 \text{ J K}^{-1} \text{mol}^{-1}$  (equivalent to a statistical weight of  $g_i = 4$ ). The thermal functions for a linear molecule were also calculated for a final thermodynamic comparison, employing the same molecular parameters as listed for the bent structure.

The molecule AuGe<sub>2</sub> has no experimentally determined molecular analogy, as does the Au<sub>2</sub>Ge molecule. As stated previously an asymmetric structure has been assumed for the AuGe<sub>2</sub> molecule. Both a linear and a bent structure have been considered. The bent molecule was assumed to have a molecular angle equal to  $110^\circ$ . An Au-Ge bond distance of 2.38 Å, with a force constant of 2.03 mdyne/Å, was again assumed. The Ge-Ge bond distance and stretching force constant were assumed equal to that assumed for the germanium dimer, namely, 2.44 Å and 2.90 mdyne/Å.<sup>24</sup> The bending force constant of this triatomic molecule was estimated as 0.27 mdyne/Å. These parameters have been assumed for both

Figure 1. Additional assumed molecular structures for the molecules Au<sub>2</sub>Ge<sub>2</sub>, AuGe<sub>3</sub>, and AuGe<sub>4</sub>.

structures. The electronic contribution for this molecule was again taken as  $11.50 \text{ J K}^{-1} \text{mol}^{-1}$ .

The calculated vibrational frequencies for the molecules Au<sub>2</sub>Ge(g) and AuGe<sub>2</sub>(g) are listed in Table II. The thermal functions for these molecules and for AuGe(g) and AuCu(g) are listed in Table III.

**Au<sub>2</sub>Ge<sub>2</sub>, AuGe<sub>3</sub>, and AuGe<sub>4</sub>.** The molecular parameters used above were again employed to calculate ideal thermodynamic functions for the molecules Au<sub>2</sub>Ge<sub>2</sub>, AuGe<sub>3</sub>, and AuGe<sub>4</sub> by using various alternate models for comparison. The first model used in each case was a linear molecular structure, which is symmetric ( $D_{\infty h}$ ) for Au<sub>2</sub>Ge<sub>2</sub> and asymmetric ( $C_{\infty v}$ ) for the AuGe<sub>3</sub> and AuGe<sub>4</sub> molecules. In every case gold was assumed monovalent.

Matrix isolation spectroscopic studies of diatomic molecules<sup>35,36</sup> indicate square-planar structures of their dimers. Thus a square-planar structure (Figure 1) was also used as a model for the molecule Au<sub>2</sub>Ge<sub>2</sub>. This structure incorporates

Table IV. Free-Energy Functions,  $-(G^\circ_T - H^\circ_0)/T$ , in  $\text{J K}^{-1} \text{mol}^{-1}$ , and Heat Content Functions,  $(H^\circ_T - H^\circ_0)$ , in  $\text{kJ mol}^{-1}$ , for the Gaseous Molecules  $\text{Au}_2\text{Ge}_2$ ,  $\text{AuGe}_3$ , and  $\text{AuGe}_4$ 

molecule (struct)		temp, K						
		298	1200	1400	1600	1800	2000	2200
$\text{Au}_2\text{Ge}_2$ (linear)	FEF	297.7	398.8	411.2	422.2	431.8	440.2	448.1
	HCF	18.69	95.81	113.2	130.6	148.0	165.4	182.9
$\text{Au}_2\text{Ge}_2$ (square planar)	FEF	317.1	416.6	428.4	438.9	448.1	456.5	464.4
	HCF	18.83	92.80	109.4	125.9	142.5	159.2	175.8
$\text{Au}_2\text{Ge}_2$ (tetrahedral)	FEF	309.0	405.1	416.9	427.2	436.4	444.8	452.3
	HCF	17.68	91.21	107.7	124.3	140.9	157.5	174.1
$\text{AuGe}_3$ (linear)	FEF	290.7	389.8	402.0	412.8	422.2	430.9	438.9
	HCF	18.01	94.85	112.2	129.6	147.0	164.4	181.9
$\text{AuGe}_3$ (tetrahedral)	FEF	304.8	397.6	409.3	419.2	428.4	436.8	444.3
	HCF	16.71	89.66	106.2	122.8	139.3	155.9	172.5
$\text{AuGe}_4$ (linear)	FEF	325.2	454.4	470.3	484.1	496.6	507.5	514.6
	HCF	23.72	122.8	145.2	167.6	190.0	212.3	234.7
$\text{AuGe}_4$ (trigonal bipyramid)	FEF	314.7	431.8	446.4	459.4	471.1	481.6	491.2
	HCF	20.53	114.6	136.1	157.6	179.1	200.7	222.2
$\text{AuGe}_4$ (tetrahedral)	FEF	340.0	465.3	480.7	494.4	506.3	517.1	526.8
	HCF	23.25	118.7	140.3	161.8	183.4	205.0	226.6

Table V. Summary of Enthalpy Changes for the Molecule  $\text{AuCu}(\text{g})$ 

homogeneous reaction	temp range, K (no. of data)	reaction enthalpy, <sup>a</sup> kJ			selected $D^\circ_{298}$ , kJ mol <sup>-1</sup> <sup>b</sup>
		second law $\Delta H^\circ_T(T, \text{K})$	second law $\Delta H^\circ_{298}$	third law $\Delta H^\circ_{298}$	
$\text{AuCu} = \text{Au} + \text{Cu}$	1641–2060 (17)	231.9 (1827)	$225.0 \pm 7.8$	$231.1 \pm 2.1$	228.0
$\text{AuCu} + \text{Au} = \text{Au}_2 + \text{Cu}$	1696–2060 (16)	-3.2 (1859)	$-3.1 \pm 7.8$	$7.0 \pm 2.0$	225.3 <sup>b</sup>
					av 226.7 $\pm$ 5.1

<sup>a</sup> Errors correspond to standard deviation. <sup>b</sup> Value of  $D^\circ_{298}(\text{Au}_2) = 223.4 \pm 3.2 \text{ kJ mol}^{-1}$  was employed.<sup>11</sup>

divalent gold and would not necessarily be considered, except for the experimental observations quoted above. An additional structure, in which the  $\text{AuGe}$  fragments are associated perpendicular to each other, also was considered to demonstrate the effect of molecular aggregation on the evaluated thermodynamic values. In this "tetrahedral" structure (Figure 1) gold is trivalent (possibility cannot be ruled out).

A second geometry assumed for the molecule  $\text{AuGe}_3$  was a cluster or aggregate similar to the tetrahedral structure described for  $\text{Au}_2\text{Ge}_2$ . A simple description of this tetrahedral model (Figure 1) is that the germanium atoms comprise an equilateral triangle with the gold atom bonded at equal atomic distance, assumed to be 2.38 Å, from each germanium atom.

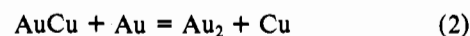
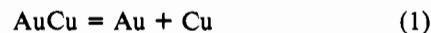
Two additional structures (Figure 1) were assumed for the  $\text{AuGe}_4$  molecule. The first is a three-dimensional structure where a central germanium atom is tetrahedrally bonded to the four remaining atoms, similar to the molecular structure of methane. The second structure is a trigonal bipyramid, in which three germanium atoms are bonded in an equilateral triangle, with the remaining Ge atom bonded at equal distance (2.44 Å) to all three below the plane of the ring and the gold atom is bonded at equal distance (2.38 Å) above the plane of the ring.

The molecular parameters employed in the calculation of the diatomic and triatomic Au-Ge molecules were again used in calculating the vibrational frequencies of the above polyatomics. Also, in order to elucidate a complete set of vibrational frequencies, we must assume additional force constants for these higher gaseous polyatomic molecules. For certain molecules a torsional force constant ( $k_T$ ) was employed, to estimate various vibrational frequencies in the available computer program, and these values are Ge-Ge-Ge-Au of 0.665 mdyne/Å, Ge-Au-Ge-Au of 0.765 mdyne/Å, and Ge-Ge-Ge-Ge of 0.565 mdyne/Å. These torsional force constants were estimated as half the sum of the two valence angle bends involved.

Many observers will not find the above assumptions valid for the clusterlike configurations and will prefer a reduction in the bonding force constants within these molecules. We

observed (though will not report) that when reaction enthalpies are calculated by employing a 50% reduction in the bond's force constant, they are by about 10 kJ mol<sup>-1</sup> smaller and that the statistical error increases by 0.5 kJ mol<sup>-1</sup> for the third-law enthalpies. Because of this increase in statistical error plus the lack of experimental results indicating the actual bond force constants in these configurations, we employed the diatomic force constants in calculating the vibrational frequency of these molecules. The electronic contribution was again taken as 11.50 J K<sup>-1</sup> mol<sup>-1</sup>, for each of the molecules. The calculated thermal functions for  $\text{Au}_2\text{Ge}_2$ ,  $\text{AuGe}_3$ , and  $\text{AuGe}_4$  are reported in Table IV, and the calculated vibrational frequencies are listed in Table IV.

**C. Evaluation of Thermodynamic Properties. AuCu.** The gas-phase equilibrium reactions considered in the evaluation of the dissociation energy for  $\text{AuCu}(\text{g})$  are



The second-law enthalpy,  $\Delta H^\circ_T$ , for reaction 1, Figure 2, was evaluated at  $231.9 \pm 7.8 \text{ kJ}$  ( $T = 1827 \text{ K}$ ), corresponding to a  $\Delta H^\circ_{298}$  of  $225.0 \pm 7.8 \text{ kJ}$ . The third-law enthalpy for the same reaction was calculated as  $\Delta H^\circ_{298} = 231.1 \pm 2.1 \text{ kJ}$ . For reaction 2 the second-law enthalpy, Figure 2, was evaluated as  $\Delta H^\circ_{1859} = -3.2 \pm 7.8 \text{ kJ}$ . The average enthalpy value obtained from a third-law evaluation was  $\Delta H^\circ_{298} = 7.0 \pm 0 \text{ kJ}$ .

The second-law entropies,  $\Delta S^\circ_{298}$ , were obtained as  $81.4 \pm 4.2$  and  $-12.4 \pm 4.2 \text{ J K}^{-1}$ , respectively, for reactions 1 and 2. The third-law entropies for the same reactions were evaluated as 84.7 and  $-6.9 \text{ J K}^{-1}$ .

For the dissociation energy (Table V) of  $\text{AuCu}(\text{g})$  we select  $D^\circ_{298} = 226.7 \pm 5.1$  ( $D^\circ_0 = 224.3$ ) kJ mol<sup>-1</sup>. Here the error term represents the estimated total uncertainty, taking all possible error sources into consideration. This dissociation energy was obtained by averaging all dissociation energies, both second and third law, for the above two reactions. The enthalpy of reaction 1 represents the dissociation energy directly.

Table VI. Summary of Enthalpy Changes for the Molecule AuGe(g)

reaction	temp range, K (no. of data)	reaction enthalpy, <sup>a</sup> kJ			selected $D_{298}^{\circ}$ , kJ mol <sup>-1</sup> <sup>198</sup>
		second law $\Delta H^{\circ}_T(T, K)$	second law $\Delta H^{\circ}_{298}$	third law $\Delta H^{\circ}_{298}$	
AuGe = Ge + Au	1408–2060 (24)	279.6 (1673)	269.7 ± 3.4	275.6 ± 1.8	272.6
AuGe + Au = Ge + Au <sub>2</sub>	1633–2060 (18)	47.3 (1822)	43.6 ± 5.8	51.5 ± 1.8	271.0 <sup>b</sup>
AuGe + Cu = Ge + CuAu	1694–2060 (17)	54.9 (1827)	51.2 ± 4.9	44.5 ± 1.3	274.3 <sup>c</sup>

av 272.6 ± 5.0

<sup>a</sup> Error corresponds to standard deviation. <sup>b</sup> Value of  $D_{298}^{\circ} = 223.4 \pm 2.1$  kJ mol<sup>-1</sup> for Au<sub>2</sub>(g).<sup>11</sup> <sup>c</sup> Value of  $D_{298}^{\circ} = 226.7 \pm 5.1$  kJ mol<sup>-1</sup> for AuCu(g), this work.

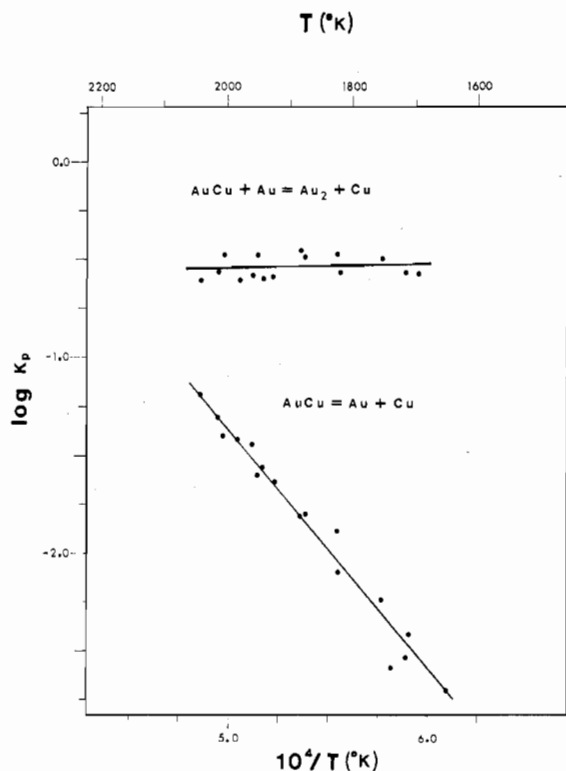


Figure 2. Second-law plots for the molecule AuCu(g).

The dissociation energy for AuCu(g) was computed from reaction 2 by employing  $D_{298}^{\circ}(\text{Au}_2) = 223.4 \pm 2.1$  ( $D_0^{\circ} = 221.3$ ) kJ mol<sup>-1</sup>.<sup>17</sup>

The selected dissociation energy for the gaseous molecule AuCu is in very good agreement with a reported literature value by Ackerman et al.<sup>25</sup> of  $D_0^{\circ}(\text{AuCu}) = 228.0 \pm 9.2$  kJ mol<sup>-1</sup>.

The value by Ackerman et al. had been based on a third-law evaluation of the reaction Au(c) + Cu(g) = AuCu(g), using fewer data (7 sets) over a more limited temperature range (1658–1798 K). These authors had to estimate the activity of gold in the liquid alloys and also had used different ionization cross sections and multiplier gains. In view of the fact that different reactions have been evaluated in the two investigations, the good agreement is particularly gratifying. In the present investigation, sets at 17 temperatures (1641–2063 K) for reaction 1 and at 16 temperatures (1686–2063 K) for reaction 2 have led to both third-law and second-law data for both reactions with very good enthalpy and entropy agreement. The higher reliability of the value for the resulting dissociation energy of AuCu(g) obtained in the present investigation is reflected in the better estimated accuracy, compared to that of Ackerman et al.<sup>25</sup> We will employ our selected value of  $D_{298}^{\circ}(\text{AuCu}) = 226.7 \pm 5.1$  in further calculations. The corresponding standard heat of formation for the gaseous molecule is obtained as  $\Delta H_{f,298}^{\circ} = 477.1 \pm 5.1$  kJ mol<sup>-1</sup>. This heat of formation was evaluated by using the value for Au(c)

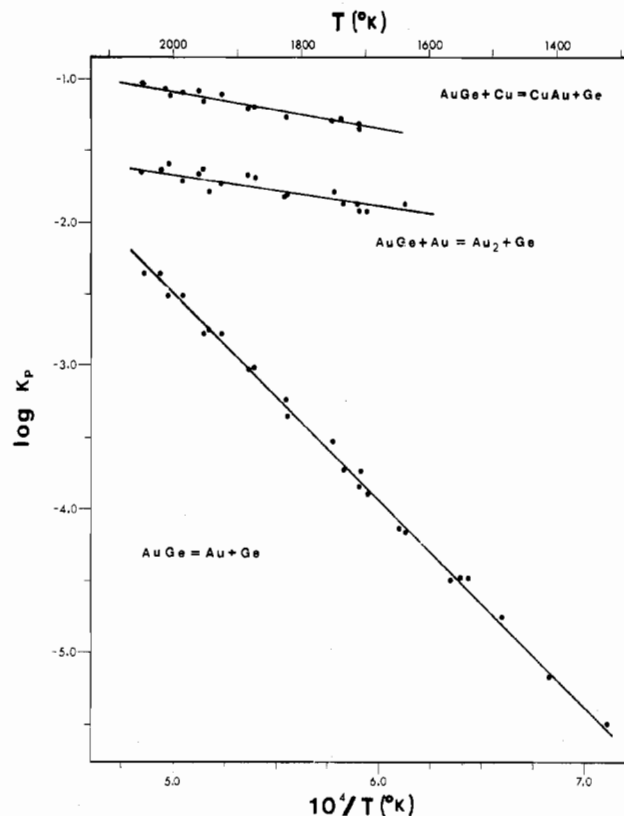
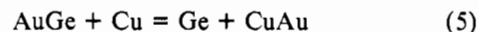
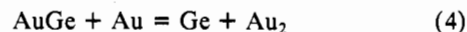
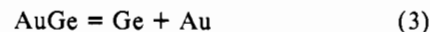


Figure 3. Second-law plots for the molecule AuGe(g).

= Au(g) equal to  $368.2 \pm 1.2$  kJ mol<sup>-1</sup> and the value for Cu(c) = Cu(g) equal to  $336.8 \pm 1.2$  kJ mol<sup>-1</sup>, as taken from Hultgren et al.<sup>23</sup>

**AuGe.** The enthalpy changes for the gaseous reactions (Table VI)



were determined by both the second- and third-law methods.

The second-law enthalpy changes,  $\Delta H^{\circ}_T$ , for reactions 3, 4, and 5 were obtained from the  $\ln K_p$  vs.  $1/T$  plot (Figure 3) as  $\Delta H^{\circ}_{1673} = 279.6 \pm 3.4$ ,  $\Delta H^{\circ}_{1822} = 47.3 \pm 5.8$ , and  $\Delta H^{\circ}_{1827} = 54.9 \pm 4.9$  kJ, respectively. The corresponding  $\Delta H^{\circ}_{298}$  values are 269.7, 43.6, and 51.2 kJ by using literature and calculated heat content functions. The corresponding second-law entropies, referenced to 298 K, are  $76.7 \pm 2.0$ ,  $-15.8 \pm 3.1$ , and  $-1.1 \pm 2.6$  J K<sup>-1</sup>.

The third-law evaluation of the above three reactions yields enthalpies ( $\Delta H^{\circ}_{298}$ ) of  $275.6 \pm 1.8$ ,  $51.5 \pm 1.8$ , and  $44.5 \pm 1.3$  kJ, for reactions 3, 4, and 5, respectively. The calculated third-law entropies ( $\Delta S^{\circ}_{298}$ ) are, respectively, 80.0,  $-11.6$ , and  $-4.7$  J K<sup>-1</sup>. The good agreement between the second- and third-law enthalpies and entropies involving the molecules

Table VII. Summary of Enthalpy Changes for the Molecule Au<sub>2</sub>Ge(g)

homogeneous reaction	temp range, K (no. of data)	reaction enthalpy, <sup>a</sup> kJ			selected $\Delta H_{a,298}^{\circ}$ , kJ mol <sup>-1</sup>
		second law $\Delta H_T^{\circ}(T, K)$	second law $\Delta H_{298}^{\circ}$	third law $\Delta H_{298}^{\circ}$	
Au <sub>2</sub> Ge = Ge + 2Au	1633–2060 (16)	573.8 (1822)			
linear			564.9 ± 12.8	589.4 ± 4.1	
bent			558.6 ± 12.8	530.6 ± 4.0	544.6
Au <sub>2</sub> Ge + Ge = 2AuGe	1686–2060 (16)	-12.1 (1854)			
linear			0.2 ± 7.1	38.0 ± 3.0	
bent			-6.2 ± 7.1	-21.1 ± 1.9	531.6 <sup>b</sup>
					av 538.1 ± 12

<sup>a</sup> Error corresponds to standard deviation. <sup>b</sup> Value of  $D_{298}^{\circ} = 272.6 \pm 5$  kJ mol<sup>-1</sup> for AuGe(g), this work.

AuGe and AuCu demonstrate the reliability of the calculated pressure constants.

The dissociation energy ( $D_{298}^{\circ}$ ) of AuGe(g) was calculated as 272.6 kJ for reaction 3, which represents directly the dissociation. Values of 271.0 and 274.3 kJ were obtained from the average of the second- and third-law enthalpies for reactions 4 and 5, respectively, by using the literature value of  $D_{298}^{\circ}(\text{Au}_2) = 223.4 \pm 2.1$  kJ mol<sup>-1</sup><sup>17</sup> and  $D_{298}^{\circ}(\text{AuCu}) = 226.7 \pm 5.1$  kJ mol<sup>-1</sup> (from the present investigation). The final selected dissociation energy of AuGe(g) is taken as the average of the above three calculated dissociation energies and is equal to  $D_{298}^{\circ} = 272.6 \pm 5.0$  kJ mol<sup>-1</sup> ( $D_0^{\circ} = 270.4$  kJ mol<sup>-1</sup>).

This average value compares favorably with a reported literature value of Neckel and Sodeck<sup>37</sup> which is equal to  $D_0^{\circ} = 273.3 \pm 14.6$  kJ mol<sup>-1</sup>. Since Neckel and Sodeck do not list the free energy functions for AuGe(g), it is not clear whether they had included the X<sub>2</sub> ( $^2\pi_{3/2}$ , 1552 cm<sup>-1</sup>) state in their computation. They discuss that this electronic state would have an effect on the free energy function that could not be neglected but state later that this effect would be within their estimated 8 kJ mol<sup>-1</sup> uncertainty. They also had a poorer second- and third-law enthalpy agreement. Furthermore there is a large uncertainty in the dissociation energy of Ge<sub>2</sub>(g), which molecule these authors utilized in their pressure-independent reaction.<sup>38</sup> We therefore consider our value as the more reliable one and will use it in the evaluation of the atomization energies of the polyatomic germanium–gold molecules.

The standard heat of formation,  $\Delta H_{f,298}^{\circ}$ , for AuGe(g) was derived at 470.0 ± 5 kJ mol<sup>-1</sup>. This value was calculated by using the  $\Delta H_{v,298}$  values for the reaction Ge(s) = Ge(g) of 374.4 ± 2.1 and 368.2 ± 1.2 kJ mol<sup>-1</sup> for the reaction Au(s) = Au(g), from Hultgren et al.<sup>23</sup>

**Au<sub>2</sub>Ge.** The second-law enthalpy changes (Figure 4),  $\Delta H_T^{\circ}$ , were determined for the gas-phase reactions



as 573.8 ± 12.9 ( $T = 1822$  K) and 12.1 ± 7.0 ( $T = 1854$  K) kJ, respectively.

The corresponding  $\Delta H_{298}^{\circ}$  values, with the assumption of a linear structure, were obtained as 564.9 and 0.2 kJ, by using the heat content change,  $\Delta(H_T^{\circ} - H_{298}^{\circ})$ . Similarly,  $\Delta H_{298}^{\circ}$  values, with the assumption of a bent configuration, were calculated as 558.6 and -6.2 kJ, for reactions 6 and 7, respectively.

Third-law enthalpies for reaction 6 were determined as 589.4 ± 4.1 and 530.6 ± 4.0 kJ for the linear and bent structures, respectively. By use of reaction 7, the third-law enthalpy obtained for the linear structure was 38.0 ± 3.0 kJ and for the bent structure was -21.1 ± 1.9 kJ. These values are summarized in Table VII.

A strong dependence of the heats of reactions on various assumed structures is clearly illustrated for the molecule

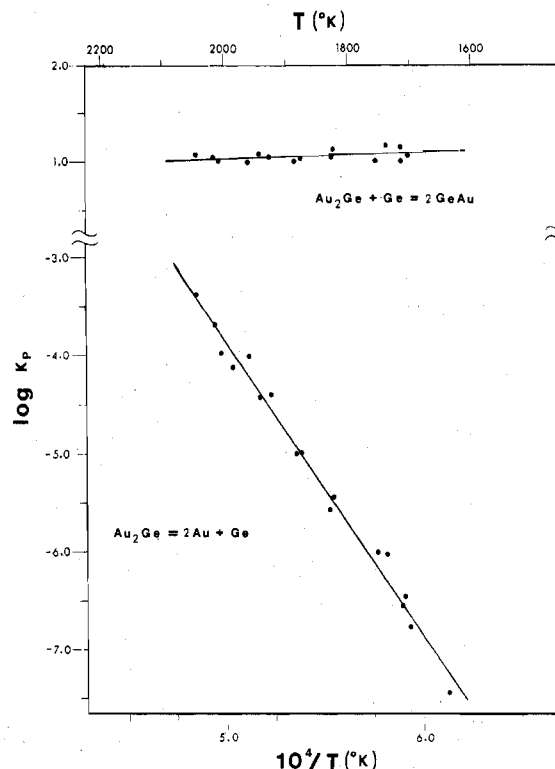


Figure 4. Second-law plots for the molecule Au<sub>2</sub>Ge(g).

Au<sub>2</sub>Ge. The evaluated  $\Delta H_{298}^{\circ}$  values for reaction 7 gives best second- and third-law agreement for the bent structure. By use of reaction 6, the difference between the second- and third-law values for the linear and the bent structure is about the same. Reaction 6 is a strongly pressure-dependent reaction. Thus, a small uncertainty in the pressure constants in evaluated heats of reactions. This fact also appears to be reflected in the larger standard deviations of reaction 6 as compared with those of reaction 7. Therefore, reaction 6 is not conclusive in demonstrating which structure may be preferred. The lower statistical error of the third-law enthalpies for the bent structure in reaction 7, as compared to the linear, also suggests the bent structure as preferred. The bent structure is further predicted by the analogy to the experimentally determined structure of GeH<sub>2</sub>, since gold and hydrogen are known have similar electronegativities for the same valence state, as discussed previously.

The corresponding second-law entropies for the bent structure, referenced to 298 K, are 191.7 ± 7.0 and 24.5 ± 3.8 J K<sup>-1</sup> for reactions 6 and 7, respectively. The corresponding third-law entropies are 176.5 and 28.0 J K<sup>-1</sup>, in fairly good agreement. These values are compared with the second-law entropies for the linear structure of 199.1 ± 6.9 and 31.9 ± 3.8 J K<sup>-1</sup> respectively for reactions 6 and 7 and the corresponding third-law entropies of 212.4 and 52.4 J K<sup>-1</sup>. Again

Table VIII. Summary of Enthalpy Changes for the Molecule AuGe<sub>2</sub>(g)

homogeneous reaction	temp range, K (no. of data)	reaction enthalpy, <sup>a</sup> kJ			selected atomization energy, kJ mol <sup>-1</sup>
		second law $\Delta H^\circ_T(T, K)$	second law $\Delta H^\circ_{298}$	third law $\Delta H^\circ_{298}$	
AuGe <sub>2</sub> = 2Ge + Au	1633-2060 (17)	572.4 (1822)			
linear			555.4 ± 14.4	571.1 ± 4.2	
bent			549.1 ± 14.5	531.1 ± 4.2	540.1
AuGe <sub>2</sub> + Au = 2AuGe	1633-2060 (17)	-6.7 (1822)			
linear			-2.6 ± 4.4	19.5 ± 2.0	
bent			-8.8 ± 4.4	-20.6 ± 1.4	530.5 <sup>b</sup>
					av 535.3 ± 10

<sup>a</sup> Error corresponds to the standard deviation. <sup>b</sup> Value of  $D^\circ_{298} = 272.6 \pm 5$  kJ mol<sup>-1</sup> for AuGe(g), this work.

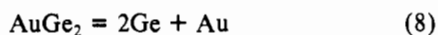
the preference for the bent structure is clearly indicated from the results for reaction 7, on the basis of the better agreement between second- and third-law results.

The atomization energy,  $\Delta H^\circ_{298}$ , of Au<sub>2</sub>Ge(g) was based on the assumed bent structure and was calculated from the average of second- and third-law enthalpies, as 544.6 kJ for reaction 6 and 531.6 kJ for reaction 7. The latter atomization energy was calculated by employing  $D^\circ_{298}(\text{AuGe}) = 272.6 \pm 5.0$  kJ, previously reported. A selected atomization energy for Au<sub>2</sub>Ge,  $\Delta H^\circ_{a,298} = 538.1 \pm 12$  kJ mol<sup>-1</sup> ( $\Delta H_{a,0} = 534.9$  kJ mol<sup>-1</sup>), was then calculated for the bent structure from the average of the above two values. The estimated uncertainties for this investigation have been included in the error term given.

The selected atomization energy of Au<sub>2</sub>Ge together with ancillary literature data<sup>23</sup> yielded the standard heat of formation.

$$\Delta H^\circ_{f,298}[\text{Au}_2\text{Ge}(\text{g})] = 572.7 \pm 12 \text{ kJ mol}^{-1}$$

**AuGe<sub>2</sub>.** The second law enthalpy changes (Figure 5),  $\Delta H^\circ_T$ , for the gas-phase reactions



were determined as  $572.4 \pm 14.4$  ( $T = 1822$  K) and  $-6.7 \pm 4.4$  ( $T = 1882$  K) kJ, respectively. The corresponding  $\Delta H^\circ_{298}$  values, on the assumption of a linear structure, were obtained as +555.4 and -2.6 kJ. Similarly,  $\Delta H^\circ_{298}$  values, on the assumption of a bent structure, were calculated as 549.1 and 8.8 kJ, for reactions 8 and 9, respectively.

Third-law enthalpies for reaction 8 were determined as  $571.1 \pm 4.2$  and  $531.1 \pm 4.2$  kJ for the linear and bent asymmetric structures, respectively. By use of reaction 9, the third-law enthalpies obtained for the linear structure were  $19.5 \pm 2.0$  kJ and for the bent structure  $-20.6 \pm 1.4$  kJ. These enthalpies are summarized in Table VIII.

Having no molecular analogy for the molecule AuGe<sub>2</sub>(g) as was available for the gaseous molecule Au<sub>2</sub>Ge, one must rely solely on the second- and third-law agreement and a variation in statistical errors of the evaluated reactions, in estimating the molecular structure of AuGe<sub>2</sub>(g). Referring to Table VIII and employing similar arguments as used for the Au<sub>2</sub>Ge(g) molecule, one observes that the bent structure for the molecule AuGe<sub>2</sub> may also be considered the preferred structure. This is indicated particularly from the somewhat better second- and third-law agreement for the pressure-independent reaction 9. The bent configuration is also indicated by the lower statistical error of the third-law enthalpies of reaction 9.

The corresponding second-law entropies ( $\Delta S^\circ_{298}$ ) for the nonlinear structure are respectively  $182.0 \pm 7.8$  and  $18.4 \pm 2.4$  J K<sup>-1</sup> for reactions 8 and 9. The third-law entropies are respectively 172 and 12.1 J K<sup>-1</sup> for the same two reactions. These results compare with the second-law entropies for the

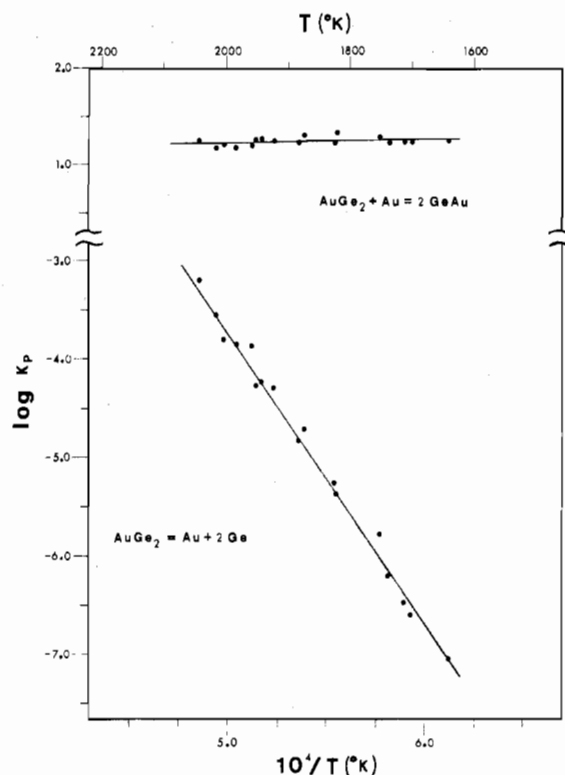


Figure 5. Second-law plots for the molecule AuGe<sub>2</sub>(g).

linear structures of  $189.3 \pm 7.8$  and  $25.8 \pm 2.4$  J K<sup>-1</sup> and the third-law entropies for the same structure of 199.4 and 37.7 J K<sup>-1</sup>. The slightly better agreement between the second- and third-law entropies for the nonlinear structure for reaction 9 may be considered as additional support of this structure, though not as conclusive as for Au<sub>2</sub>Ge(g).

A selected atomization energy for the gaseous bent molecule AuGe<sub>2</sub>, referenced to 298 K,  $\Delta H^\circ_{a,298} = 535.3 \pm 10.0$  kJ mol<sup>-1</sup> ( $\Delta H^\circ_{a,0} = 531.9$  kJ mol<sup>-1</sup>), was similarly evaluated for the molecule Au<sub>2</sub>Ge(g). The estimated uncertainty in the thermal functions, pressure calibration, and temperature measurements for this investigation have been included in the error term given here.

The heat of formation,  $\Delta H^\circ_{f,298}$ , of gaseous AuGe<sub>2</sub> was derived as  $581.5 \pm 10.0$  kJ mol<sup>-1</sup> by using ancillary data from the literature.<sup>23</sup>

**Au<sub>2</sub>Ge<sub>2</sub>.** The equilibrium reaction



was studied, and the calculated third-law enthalpies,  $\Delta H_{298}$ , were determined (Table IX) as  $388.6 \pm 2.8$  kJ for the linear structure,  $313.8 \pm 3.5$  kJ for the square-planar structure, and  $338.7 \pm 3.2$  kJ for the tetrahedral structure. The corresponding third-law entropies,  $\Delta S^\circ_{298}$ , are 196.7, 156.1 and 168.0 K<sup>-1</sup>.



Table IX. Third-Law Enthalpies for the Reaction  $\text{Au}_2\text{Ge}_2(\text{g}) = 2\text{AuGe}(\text{g})$ 

data set no. <sup>a</sup>	T, K	log $K_p$	$-\Delta[(G^\circ_T - H^\circ_{298})/T], \text{ J K}^{-1}$			$\Delta H^\circ_{298}, \text{ kJ}$			
			linear	sq planar	tetrahedral	linear	sq planar	tetrahedral	
14	1954	0.387	45.3	36.4	39.3	386.8	313.3	337.9	
15	2010	0.260	45.3	36.4	39.3	392.8	317.3	342.5	
16	1947	0.548	45.3	36.4	39.3	391.6	318.3	342.7	
22	1934	0.523	45.3	36.4	39.3	388.1	315.2	337.5	
24	2023	-0.013	45.3	36.4	39.2	384.7	308.8	334.1	
25	2060	-0.121	45.3	36.4	39.3	387.3	310.1	335.9	
						av	$388.6 \pm 2.8$	$313.8 \pm 3.5$	$338.7 \pm 3.2$

<sup>a</sup> Data set numbers correspond to data tabulated in the supplementary material. <sup>b</sup> Error corresponds to standard deviation.

Table X. Third-Law Enthalpies for the Reaction  $\text{AuGe}_3(\text{g}) + 2\text{Au}(\text{g}) = 3\text{AuGe}(\text{g})$ 

data set no. <sup>a</sup>	T, K	log $K_p$	$-\Delta[(G^\circ_T - H^\circ_{298})/T], \text{ J K}^{-1}$		$\Delta H^\circ_{298}, \text{ kJ}$			
			linear	tetra- hedral	linear	tetrahedral		
13	1911	2.00	20.2	18.8	87.8	77.7		
15	2010	2.12	20.1	18.7	86.8	76.5		
16	1947	2.09	20.2	18.8	85.9	75.8		
22	1934	2.10	20.2	18.8	84.9	74.7		
23	1985	2.08	20.1	18.7	87.3	77.5		
24	2023	2.18	20.1	18.7	84.9	74.6		
25	2060	2.35	20.1	18.7	79.8	69.5		
						av	$85.4 \pm 2.5$	$75.3 \pm 2.6$

<sup>a</sup> Data set number corresponds to data tabulated in the supplementary material. <sup>b</sup> Error corresponds to standard deviation.

The evaluated second-law enthalpies,  $\Delta H^\circ_{298}$ , for reaction 10 are  $415.8 \pm 58.8$  kJ for the linear structure,  $409.7 \pm 58.8$  kJ for the square-planar structure and  $409.2 \pm 58.8$  kJ for the tetrahedral structure. No major significance can be placed on these second-law values, because of the limited data and short temperature range involved. These values are only reported for comparison to support the more reliable third-law data, but a preference for the linear structure appears indicated.

Consideration of the variance in the standard deviation of the calculated third-law reaction enthalpies produced by employing different free-energy functions can also be used to analyze the correctness of the chosen free-energy functions. As the various estimated molecular parameters differ from the unknown true value, a trend is developed with temperature within the free-energy functions. The greater the trend becomes the larger the standard deviation in the calculated third-law enthalpies. In reference to Table IX, one observes the smallest standard deviation for the linear molecule  $\text{Au}_2\text{Ge}_2(\text{g})$ .

The germanium dimer is believed to exist in a  $^3\Sigma$  ground state,<sup>28</sup> which contains two unpaired electrons, one at each atom. The availability of these unpaired electrons enhances the likelihood that the gold atoms will bond more readily to different germanium atoms. Because the multiple bonds between the Ge atom will probably be unaffected by the addition of two gold-germanium bonds. This structure would then be isoelectronic to acetylene ( $\text{C}_2\text{H}_2$ ), which is linear.

Table XI. Third-Law Enthalpies for the Reaction  $\text{AuGe}_4(\text{g}) + 3\text{Au}(\text{g}) = 4\text{AuGe}(\text{g})$ 

data set no. <sup>a</sup>	T, K	log $K_p$	$-\Delta[(G^\circ_T - H^\circ_{298})/T], \text{ J K}^{-1}$			$\Delta H^\circ_{298}, \text{ kJ}$			
			linear	trig bipyramid	tetrahedral	linear	trig bipyramid	tetrahedral	
16	2010	1.83	37.4	50.2	32.9	153.7	211.7	135.6	
23	1985	1.52	39.7	52.4	35.3	163.6	220.7	145.6	
						av	$158.7 \pm 4.9$	$216.2 \pm 4.5$	$140.6 \pm 5.0$

<sup>a</sup> Data set number corresponds to data tabulated in the supplementary material. <sup>b</sup> Error corresponds to deviation from the arithmetic mean.

Therefore, the free-energy function calculated by assuming a symmetric linear structure best represents the gaseous molecule  $\text{Au}_2\text{Ge}_2$ .

These third-law enthalpies listed in Table IX yielded atomization energies for the assumed linear, square-planar, and tetrahedral structures of  $934 \pm 14$  ( $\Delta H^\circ_{a,0} = 927$ ),  $859 \pm 18$  ( $\Delta H^\circ_{a,0} = 853$ ), and  $884 \pm 16$  ( $\Delta H^\circ_{a,0} = 877$ ) kJ, respectively, by using  $D^\circ_{298}(\text{AuGe}) = 272.6$  kJ mol<sup>-1</sup>. We recommend the value based on the linear structure as the selected atomization energy. The standard heat of formation, based on the preferred linear structure, was derived as  $551 \pm 14$  kJ mol<sup>-1</sup>. Literature enthalpies used in obtaining the heat of formation came from Hultgren et al.<sup>23</sup>

**AuGe<sub>3</sub> and AuGe<sub>4</sub>.** The third-law enthalpies, referenced to 298 K, for the gas-phase reactions



have been evaluated as  $85.4 \pm 2.1$  kJ for the linear molecule and  $74.3 \pm 2.6$  kJ for the tetrahedral molecule, by employing reaction 11. For reaction 12 the third-law enthalpies were obtained as  $158.7 \pm 4.9$  kJ for the linear structure,  $216.2 \pm 4.5$  kJ for the trigonal-bipyramidal structure, and  $140.6 \pm 5.0$  kJ for the tetrahedral structure. These reaction enthalpy calculations are summarized in Tables X and XI. The third-law reaction entropies corresponding to a linear molecule of  $\text{AuGe}_3(\text{g})$  and  $\text{AuGe}_4(\text{g})$  were obtained as 92.6 and 126.7 J K<sup>-1</sup>, respectively, for reactions 11 and 12.

In coming to a decision about the structures of  $\text{AuGe}_3(\text{g})$  and  $\text{AuGe}_4(\text{g})$ , we considered no reliable second-law enthalpy changes for the higher polyatomic Ge-Au molecules since the reciprocal temperature range is limited in its extent. We then considered only the calculated third-law enthalpies and molecular analogies for some insight into the more likely structure of these polyatomic molecules.

Theoretical calculations by Anderson<sup>6</sup> have demonstrated that for the five-atom molecules of the group 4A,B elements, in particular  $\text{Ti}_5$  and  $\text{Sn}_5$ , the trigonal-bipyramidal structure is probably the most stable form. This same structure is believed to be the more stable form for the molecule  $\text{Ge}_5$ , which demonstrates similar bonding to  $\text{Sn}_5$ . Therefore, a simple replacement of one germanium atom by gold may not disrupt this more stable configuration. The same structure, trigonal bipyramidal, also shows the smallest statistical error of the three structures considered for the molecule  $\text{AuGe}_4(\text{g})$ . The



Table XII. Summary of Enthalpy Changes for the Molecule  $\text{Ge}_2(\text{g})$ 

reaction	temp range, K (no. of data)	reaction enthalpy, <sup>a</sup> kJ			selected $D^\circ_{298}$ , kJ mol <sup>-1</sup>
		second law $\Delta H^\circ_T$ (T, K)	second law $\Delta H^\circ_{298}$	third law $\Delta H^\circ_{298}$	
$\text{Ge}_2 = 2\text{Ge}$	1528–2060 (17)	277.3 ± 6.0 (1787)	254.8 ± 6.0	266.5 ± 2.1	262.6 <sup>b</sup>
$\text{Ge}_2 + \text{Au} = \text{Ge} + \text{AuGe}$	1528–2060 (17)	-12.2 ± 3.3 (1787)	-24.3 ± 3.3	-9.4 ± 1.5	258.2 <sup>b,c</sup>
					av 260.4 ± 10

<sup>a</sup> Error corresponds to standard deviation. <sup>b</sup> Average of second and third law calculated atomization energy, giving twice the weight to the more reliable third law. <sup>c</sup> Value of  $D^\circ_{298} = 272.6 \pm 5$  kJ mol<sup>-1</sup> for AuGe(g) was employed, this work.

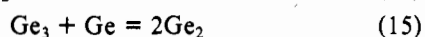
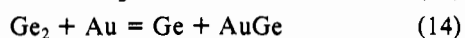
enthalpy changes for the molecule  $\text{AuGe}_3$  is calculated by using only two data points, and any conclusion drawn from the statistical error alone can only be speculative. The final demonstration of this molecule's structure will be left to theorists and spectroscopists.

Neither of the two models considered for  $\text{AuGe}_3(\text{g})$  is indicated more favorable from the thermodynamic calculations or molecular analogy. We thus propose the linear structure as the preferred one, mainly because of the preference of monovalent gold.

Calculated atomization energies,  $\Delta H^\circ_{a,298}$ , for the linear  $\text{AuGe}_3(\text{g})$  molecule was obtained as  $903 \pm 20$  ( $\Delta H^\circ_{a,0} = 897$ ) kJ mol<sup>-1</sup> and for the trigonal-bipyramidal  $\text{AuGe}_4(\text{g})$  molecule was obtained as  $1307 \pm 30$  ( $\Delta H^\circ_{a,0} = 1296$ ) kJ mol<sup>-1</sup>. These were evaluated by assuming a  $D^\circ_{298}(\text{AuGe}) = 272.6 \pm 5.0$  kJ mol<sup>-1</sup>. Here the error term corresponds to an estimated overall uncertainty.

Standard heats of formation,  $\Delta H^\circ_{f,298}$ , for these two molecules were derived as  $588 \pm 20$  and  $559 \pm 30$  kJ mol<sup>-1</sup>, for  $\text{AuGe}_3$  and  $\text{AuGe}_4$ , respectively. Literature sublimation enthalpies for gold and germanium used in obtaining these values came from Hultgren et al.<sup>23</sup>

$\text{Ge}_2$ ,  $\text{Ge}_3$ , and  $\text{Ge}_4$ . Several equilibrium reactions may be considered in an analysis of the reaction enthalpies for the different polyatomic germanium molecules. Of particular interest in this investigation were the reactions



We have studied reactions 13 and 14 over a temperature range 1578–2060 K (17 data sets). The second-law enthalpy changes at temperature 1787 K,  $\Delta H^\circ_T = 277.3 \pm 6.0$  and  $\Delta H^\circ_T = -12.2 \pm 3.3$  kJ, respectively, for reactions 13 and 14, were obtained. These enthalpies correspond to  $\Delta H^\circ_{298} = 254.8 \pm 6.0$  kJ and  $\Delta H^\circ_{298} = -24.3 \pm 3.3$  kJ, respectively. The calculated third-law enthalpy, Table XII, changes for the same two reactions are  $\Delta H^\circ_{298} = 266.5 \pm 2.1$  kJ and  $\Delta H^\circ_{298} = -9.4 \pm 1.5$  kJ, respectively.

The corresponding second- and third-law entropies for reaction 13, respectively, are  $78.5 \pm 3.7$  and  $86.3$  J K<sup>-1</sup>, and for reaction 14 are  $-3.3 \pm 1.8$  and  $+6.3$  J K<sup>-1</sup>. Because the number of data is slightly limited for the extended temperature range employed, the second-law enthalpy calculated here may be less reliable than the evaluated third-law enthalpy. Therefore, a selected dissociation energy is calculated from the above two reactions by employing the average of both the second and third law, giving twice the statistical weight to the third-law value. These values are respectively for reactions 13 and 14  $D^\circ_{298} = 262.6 \pm 10$  ( $D^\circ_0 = 257.2$ ) kJ mol<sup>-1</sup> and  $D^\circ_{298} = 258.2 \pm 10$  ( $D^\circ_0 = 254.3$ ) kJ mol<sup>-1</sup>. The latter dissociation energy was calculated by using the evaluated  $D^\circ_{298}(\text{AuGe}) = 272.6 \pm 5.0$  kJ mol<sup>-1</sup> (this work). A final value for the dissociation energy of  $\text{Ge}_2(\text{g})$  is taken as the average of these two previous values and is  $D^\circ_{298} = 260.4 \pm 10$  ( $D^\circ_0 = 255.7$ ) kJ mol<sup>-1</sup>.

Table XIII. Third-Law Enthalpies for the Reaction  $\text{Ge}_3(\text{g}) + \text{Ge}(\text{g}) = 2\text{Ge}_2(\text{g})$ 

data set no. <sup>a</sup>	T, K	-log $K_p$	$-\Delta[(G^\circ_T - H^\circ_{298})/T],$ J K <sup>-1</sup>	$\Delta H^\circ_{298},$ <sup>b</sup> kJ
11	1804	1.01	7.52	92.0
12	1866	0.93	7.43	91.5
13	1911	0.89	7.37	92.0
14	1954	0.94	7.31	95.4
15	2010	0.87	7.25	94.9
16	1947	0.94	7.32	95.3
20	1801	1.07	7.52	93.8
21	1856	1.05	7.44	95.6
22	1934	0.90	7.34	93.3
				av 93.8 ± 1.5

<sup>a</sup> Data set number corresponds to data tabulated in the supplementary material. <sup>b</sup> Error corresponds to standard deviation.

Table XIV. Third-Law Enthalpies for the Reaction  $\text{Ge}_4(\text{g}) = 2\text{Ge}_2(\text{g})$ 

data set no. <sup>a</sup>	T, K	-log $K_p$	$-\Delta[(G^\circ_T - H^\circ_{298})/T],$ J K <sup>-1</sup>	$\Delta H^\circ_{298},$ <sup>b</sup> kJ
12	1866	4.25	37.6	445.9
13	1911	3.78	37.6	439.1
14	1954	3.62	37.5	442.7
15	2010	3.44	37.5	447.9
16	1947	3.83	37.5	448.9
21	1856	4.37	37.6	447.7
22	1934	3.80	37.6	445.0
				av 445.3 ± 3.2

<sup>a</sup> Data set number corresponds to data tabulated in the supplementary material. <sup>b</sup> Error corresponds to standard deviation.

The equilibrium dissociation reaction, reaction 13, has been studied mass spectroscopically by Drowart et al.<sup>24</sup> Kant and Strauss<sup>39</sup> and Neckel and Sodeck.<sup>37</sup> The dissociation energies  $D^\circ_0(\text{Ge}_2)$  determined from these studies were  $267.8 \pm 21$ ,  $272.0 \pm 21$ , and  $269.9 \pm 21$  kJ mol<sup>-1</sup>, respectively. If we adjust for the same free-energy functions as those in literature,<sup>24,39</sup> and in the present investigation, the value by Neckel and Sodeck becomes  $271.4 \pm 21$  kJ mol<sup>-1</sup>. All these literature values are higher than the value for  $D^\circ_0(\text{Ge}_2) = 255.7 \pm 10$  kJ mol<sup>-1</sup> obtained in the present investigation, although our value falls within the stated error limits.

Drowart et al.<sup>24</sup> used 10–15-eV ionizing electrons, Kant and Strauss<sup>39</sup> used 20- or 70-eV electrons, noting the independence of the  $I(\text{Ge}_2^+)/I(\text{Ge}^+)$  ratio on the electron energy, and Neckel and Sodeck used 10.6 eV. These compare with the 20-eV electron energy used by us. We did note the possibility of some arbitrary fragmentation correction assuming some fragmentation for the germanium and germanium-containing polyatomic molecules, and improvement between second- and third-law enthalpies by 2 kJ was obtained. The average dissociation calculated from these corrected values was still lower than the values reported in literature. We did not apply any fragmentation correction to the reported value, because the other researchers did not report any fragmentation in the pure germanium systems and we had no strong justification

Table XV. Summary of Atomization Energy and Standard Heats of Formation of the Experimentally Observed Gaseous Molecules

species	$\Delta H_{a,298}^{\circ}$ , <sup>a</sup> kJ mol <sup>-1</sup> , this study	$\Delta H_{a,0}^{\circ}$ , kJ mol <sup>-1</sup> , this study	$\Delta H_{a,0}$ , <sup>b</sup> lit.	$\Delta H_{f,298}^{\circ}$ , kJ mol <sup>-1</sup> , this study	$\Delta H_{f,0}^{\circ}$ , kJ mol <sup>-1</sup> , this study
AuGe	272.6 ± 5.0	270.5	273.3 ± 15	470.0 ± 5.0	469.3
Au <sub>2</sub> Ge					
linear	570.8 ± 14	567.5			
bent	538.1 ± 12	534.9		572.7 ± 12	572.6
AuGe <sub>2</sub>					
linear	558.5 ± 12	555.6			
bent	535.3 ± 10	531.9		581.5 ± 10	579.3
Au <sub>2</sub> Ge <sub>2</sub>					
linear	934 ± 14	927		551 ± 14	552
sq planar	859 ± 18	853			
tetrahedral	884 ± 16	877			
AuGe <sub>3</sub>					
linear	903 ± 20	897		582 ± 20	586
tetrahedral	893 ± 20	865			
AuGe <sub>4</sub>					
linear	1251 ± 32	1242			
trig bipyramid	1307 ± 30	1295		559 ± 30	560
tetrahedral	1231 ± 32	1223			
AuCu	226.7 ± 5.1	224.3	228.0 ± 9	477.1 ± 5.1	478.1
Ge <sub>2</sub>	260.4 ± 10	255.7	269.7 ± 21	488.4 ± 10	487.4
Ge <sub>3</sub>	637 ± 20	627	644.4 ± 21	486 ± 20	488
Ge <sub>4</sub>	989 ± 22	977	1010.4 ± 30	509 ± 22	510

<sup>a</sup> Error corresponds to estimated overall uncertainty. <sup>b</sup> Refer to text for references.

to do so. A selected dissociation energy,  $D^{\circ}_{298}(\text{Ge}_2) = 271.4 \pm 17$  ( $D^{\circ}_0 = 266.4$ ) kJ mol<sup>-1</sup>, has been obtained as the average of all literature values and our value. This selected value has been employed in evaluating the atomization energies of Ge<sub>3</sub>(g) and Ge<sub>4</sub>(g) in the present investigation.

The atomization energies of the gaseous molecules Ge<sub>3</sub> and Ge<sub>4</sub> have been subject to evaluation of experimental data by both Kant and Strauss<sup>39</sup> and Drowart et al.<sup>24</sup> These investigations were limited to narrow temperature ranges and a limited number of data. The calculated third-law atomization energies from Kant and Strauss<sup>39</sup> are  $\Delta H^{\circ}_{a,0}(\text{Ge}_3) = 648.5 \pm 17$  kJ mol<sup>-1</sup> and  $\Delta H^{\circ}_{a,0}(\text{Ge}_4) = 1016.7 \pm 33$  kJ mol<sup>-1</sup>, and from Drowart et al.<sup>24</sup> the corresponding values are  $640.2 \pm 21$  and  $1004.2 \pm 22$  kJ mol<sup>-1</sup>, respectively. These values refer to an assumed linear structure, which is indicated by Kant and Strauss to be probably the preferred structure, as compared to cyclic structures. The present evaluations have therefore been made by assuming linear structures of these molecules.

The evaluated third-law enthalpies for reaction 15 are listed in Table XIII. The average third-law enthalpy change for this reaction is obtained as  $\Delta H^{\circ}_{298} = 93.8 \pm 1.5$  kJ. Combining this value and the value  $D^{\circ}_{298}(\text{Ge}_2) = 271.4 \pm 17$  kJ mol<sup>-1</sup>, we obtained an evaluated  $\Delta H_{a,298}(\text{Ge}_3) = 636.6 \pm 20$  kJ mol<sup>-1</sup>. An average third-law enthalpy change for reaction 16 was evaluated as  $\Delta H^{\circ}_{a,298} = 445.3 \pm 3.2$  kJ (Table XIV). The atomization energy of  $\Delta H^{\circ}_{a,298}(\text{Ge}_4) = 988.9 \pm 22$  ( $\Delta H^{\circ}_{a,0} = 977.2$ ) kJ mol<sup>-1</sup> was obtained from  $\Delta H(\text{R16})$  by employing again the above  $D^{\circ}_{298}(\text{Ge}_2)$ . The above error terms associated with the atomization energies correspond to estimated overall errors, and the remaining errors represent standard deviations.

As in the case of the Ge<sub>2</sub> molecule, the atomization energies of Ge<sub>3</sub> and Ge<sub>4</sub> are lower, but within the stated error limits of the corresponding literature values.

The standard heats of formation,  $\Delta H^{\circ}_{f,298}$ , of Ge<sub>2</sub>, Ge<sub>3</sub>, and Ge<sub>4</sub> were derived by using ancillary data from the literature,<sup>23</sup>  $\Delta H^{\circ}_{f,298}(\text{Ge}(g)) = 374.4 \pm 21$  kJ mol<sup>-1</sup>. The calculated heats of formation are  $477.4 \pm 17$  (based on  $D^{\circ} = 271.4 \pm 17$  kJ mol<sup>-1</sup>),  $486.9 \pm 20$ , and  $509.9 \pm 22$  kJ mol<sup>-1</sup>, respectively.

### Summary and Conclusion

The extensive data reported in the previous discussion are summarized in Table XV. This includes the previously unreported gaseous molecules Au<sub>2</sub>Ge (bent,  $538.1 \pm 12$ ), AuGe<sub>2</sub> (bent,  $535.3 \pm 10$ ), Au<sub>2</sub>Ge<sub>2</sub> (linear,  $934 \pm 14$ ), AuGe<sub>3</sub>

Table XVI. Correlation of an Estimated Gold Binding Energy of Germanium Clusters

molecule (struct)	$H^{\circ}_{a,0}(\text{AuGe}_n) - H^{\circ}_{a,0}(\text{Ge}_n)$ , kJ mol <sup>-1</sup>
AuGe	270.5
AuGe <sub>2</sub> (bent)	276.2
AuGe <sub>3</sub> (linear)	270
AuGe <sub>4</sub> (trigonal bipyramid)	318

(linear,  $903 \pm 20$ ), and AuGe<sub>4</sub> (trigonal bipyramid,  $1307 \pm 30$ ). Thus, it is seen that the geometry and structure chosen for a given molecule have a significant effect on its atomization energy.

It would be interesting to compare the relative strengths of the bond between an Au atom and the various germanium clusters. In Table XVI, the quantities  $\Delta H^{\circ}_{a,0}(\text{AuGe}_n) - \Delta H^{\circ}_{a,0}(\text{Ge}_n)$  are presented for the gold–germanium clusters studied in this investigation. In these computations, the atomization energies for Ge<sub>n</sub>(g) used are from the present work and those for AuGe<sub>n</sub>(g) correspond to the preferred structures. One observes that for the molecules AuGe, AuGe<sub>2</sub>, and AuGe<sub>3</sub> the gold to germanium cluster association energy is relatively constant but for the molecule AuGe<sub>4</sub> the stability is enhanced. This increase in stability may be interpreted as arising from clustering within the molecule, but without further work, namely, the determination of accurate second-law enthalpies and the extension of the investigation to higher clusters, no conclusive analysis leading to a limiting value for the binding energy of an Au atom to “bulk” Ge is possible.

For the linear molecule Au<sub>2</sub>Ge<sub>2</sub> a significantly higher Au–Ge binding bond energy than that in the diatomic molecule AuGe is obtained. This is also observed in other metal–group 4A molecules, e.g., Au<sub>2</sub>Sn<sub>2</sub><sup>11</sup> and Li<sub>2</sub>Si<sub>2</sub>.<sup>40</sup> All these molecules are quasi-isoelectronic with acetylene for which the stability is attributed to the strong triple bond between the carbon atoms, as well as the bond strengthening of the H–C bond through hybridization. Thus triple bond formation between the group 4 elements in Au<sub>2</sub>Ge<sub>2</sub>, Li<sub>2</sub>Si<sub>2</sub>, and Au<sub>2</sub>Sn<sub>2</sub> is suggested.

The atomization energy data obtained in the present investigation hopefully will stimulate structural investigations and theoretical calculations which would permit more meaningful conclusions regarding the trends in the binding

energies of gold as a function of germanium cluster size.

**Acknowledgment.** We gratefully acknowledge the continued support of the Robert A. Welch Foundation (Grant A-387) and the National Science Foundation (Grant No. CHE-10075 A 02 and CHE 78-08711). The authors are grateful to Dr. S. K. Gupta for his helpful discussions.

**Registry No.** Au<sub>2</sub>, 12187-09-6; AuCu, 12006-51-8; AuGe, 12256-41-6; Au<sub>2</sub>Ge, 67701-68-2; AuGe<sub>2</sub>, 67701-72-8; Au<sub>2</sub>Ge<sub>2</sub>, 67701-69-3; AuGe<sub>3</sub>, 67701-70-6; AuGe<sub>4</sub>, 67701-71-7; Ge<sub>2</sub>, 12596-05-3; Ge<sub>3</sub>, 61349-37-9; Ge<sub>4</sub>, 12184-87-1.

**Supplementary Material Available:** A table of the experimental ion currents (5 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) This work was performed as part of a requirement for a Master of Science degree (J.E.K., Texas A&M University, 1978).
- (2) J. E. McDonald, *Am. J. Phys.*, **30**, 870 (1962); **31**, 31 (1963).
- (3) P. P. Wegener and J. Y. Parlange, *Naturwissenschaften*, **57**, 525 (1970).
- (4) J. J. Burton, *Acta Metall.*, **21**, 1225 (1973).
- (5) F. F. Abraham, "Homogeneous Nucleation Theory", Academic Press, New York, 1974.
- (6) A. B. Anderson, *J. Chem. Phys.*, **63**, 4430 (1975); **64**, 4046 (1976).
- (7) R. C. Baetzold and R. E. Mack, *J. Chem. Phys.*, **62**, 1513 (1975).
- (8) J. H. Sinfelt, *J. Catal.*, **29**, 308 (1973); *Acc. Chem. Res.*, **10**, 15 (1977).
- (9) A. B. Anderson and R. Hoffmann, *J. Chem. Phys.*, **61**, 4545 (1974).
- (10) R. van Hardevel and F. Hartog, *Adv. Catal.*, **22**, 75 (1972).
- (11) K. A. Gingerich, D. L. Cocke, and U. V. Choudary, *Inorg. Chim. Acta*, **14**, L47 (1975).
- (12) K. A. Gingerich and J. E. Kingcade, *Inorg. Chim. Acta*, **29**, L229 (1978).
- (13) K. A. Gingerich, *J. Cryst. Growth*, **9**, 31 (1971); *J. Chem. Phys.*, **49**, 14 (1968).
- (14) R. T. Grimley in "Characterization of High Temperature Vapors", J. L. Margrave, Ed., Wiley-Interscience, New York, 1971, pp 195-243.
- (15) J. Drowart and P. Goldfinger, *Angew. Chem.*, **79**, 589 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 581 (1967).
- (16) J. E. Kingcade, K. A. Gingerich, and U. V. Choudary, *J. Phys. Chem.*, **82**, 49 (1978).
- (17) J. Kordis, K. A. Gingerich, and R. J. Seyse, *J. Chem. Phys.*, **61**, 5114 (1974).
- (18) R. F. Pottie, D. L. Cocke, and R. A. Gingerich, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 41 (1973).
- (19) J. B. Mann, *Recent Dev. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc.*, 814-819 (1970).
- (20) D. R. Stull and H. Prophet in "Characterization of High Temperature Vapors", J. L. Margrave, Ed., Wiley-Interscience, New York, 1967, pp 359-424.
- (21) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).
- (22) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941); E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955.
- (23) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, "Selected Values of Thermodynamic Properties of the Elements", American Society for Metals, Metals Park, Ohio, 1973.
- (24) J. Drowart, G. DeMaria, A. J. H. Boerboom, and M. G. Inghram, *J. Chem. Phys.*, **30**, 308 (1959).
- (25) M. Ackerman, F. E. Stafford, and J. Drowart, *J. Chem. Phys.*, **33**, 1784 (1960).
- (26) R. Houdart and J. Schamps, *J. Phys. B*, **6**, 2478 (1973).
- (27) R. F. Barrow, W. J. M. Gissane, and D. N. Travis, *Nature (London)*, **201**, 603 (1964).
- (28) C. G. Cheetham and R. F. Barrow, *Adv. High Temp. Chem.*, **1** (1964).
- (29) G. R. Smith and W. A. Guillory, *J. Chem. Phys.*, **56**, 1423 (1972).
- (30) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).
- (31) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **52**, 2594 (1970).
- (32) G. Herzberg, "The Spectra and Structure of Simple Free Radicals", Cornell University Press, Ithaca, N.Y., 1971.
- (33) L. Andrews and D. L. Frederick, *J. Am. Chem. Soc.*, **92**, 775 (1970).
- (34) W. A. Guillory and C. E. Smith, *J. Chem. Phys.*, **53**, 1661 (1970).
- (35) A. J. Downs and S. C. Peake, *Mol. Spectrosc.*, **1**, 523 (1973).
- (36) B. M. Chadwick, *Mol. Spectrosc.*, **3**, 281 (1975).
- (37) A. Neckel and G. Sodeck, *Monatsh. Chem.*, **103**, 367 (1972).
- (38) The enthalpy reported by Neckel and Sodeck has been based on a third-law evaluation of the reaction  $\text{Ge}_2 + \text{Au} = \text{AuGe} + \text{Ge}$ , with  $D^\circ_0(\text{Ge}_2) = 269.9 \pm 21 \text{ kJ mol}^{-1}$ , using nine data sets (1720-1872 K which yielded  $D^\circ_0(\text{AuGe}) = 269.9 \pm 14.6 \text{ kJ mol}^{-1}$ ) and on the evaluation of the equilibrium  $\text{AuGe} = \text{Au} + \text{Ge}$  in six experiments using Ge-Au melts of different composition. Here the partial pressures of the atomic species were determined activities of Ge and Au. The resulting third-law dissociation energy was  $276.6 \pm 13.4 \text{ kJ mol}^{-1}$ . Not considered were second-law enthalpies  $290.8 \pm 12.6$  and  $286.2 \pm 12.6$ , respectively.
- (39) A. Kant and B. H. Strauss, *J. Chem. Phys.*, **45**, 822 (1966).
- (40) H. R. Ihle, C. H. Wu, and K. F. Zmbor, personal communication, presented at the 7th International Meeting on Mass Spectroscopy, Florenz, 1976.

Contribution from the Institut de Recherche sur la Catalyse, 69626 Villeurbanne, France, the Istituto di Chimica Generale e Inorganica dell'Università, Centro CNR, 20133 Milano, Italy, and the Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S-1A4, Canada

## Surface-Supported Metal Cluster Carbonyls. Chemisorption Decomposition and Reactivity of Rh<sub>6</sub>(CO)<sub>16</sub> Supported on Alumina, Silica-Alumina, and Magnesia

A. K. SMITH, F. HUGUES, A. THEOLIER, J. M. BASSET,\* R. UGO, G. M. ZANDERIGHI, J. L. BILHOU, V. BILHOU-BOUGNOL, and W. F. GRAYDON

Received August 17, 1978

The behavior of Rh<sub>6</sub>(CO)<sub>16</sub> on the surface of inorganic oxides (alumina, magnesia, and silica-alumina) has been found to be strongly dependent on the mode of impregnation and on the water content of the support. On alumina it is possible to maintain the molecular nature of the cluster provided the water content of the alumina is low; otherwise the OH groups of the support are at the origin of a ready oxidation of the cluster resulting in a rhodium(I) carbonyl species. The rhodium(I) carbonyl species reacts with CO in the presence of excess water to give back the cluster Rh<sub>6</sub>(CO)<sub>16</sub>. Rh(CO)<sub>2</sub>Cl<sub>2</sub> supported on alumina also reacts with CO in the presence of excess water to give Rh<sub>6</sub>(CO)<sub>16</sub>. A facile reduction of the rhodium(I) carbonyl species, obtained from oxidation of Rh<sub>6</sub>(CO)<sub>16</sub>, under hydrogen or excess water in the absence of CO leads to the formation of metallic rhodium together with an "intramolecular" rearrangement of a linear to a doubly bridged carbonyl ligand. It is possible to regenerate the rhodium(I) surface carbonyl species with oxygen followed by carbon monoxide. Infrared data for Rh<sub>6</sub>(CO)<sub>16</sub> supported on alumina, magnesia, and silica-alumina indicate an electronic interaction between the support and the cluster, the rhodium(I) carbonyl species, or the metallic species obtained upon reduction of rhodium(I). A catalytic cycle is proposed which accounts for the water gas shift reaction carried out on the cluster frame and its oxidation products.

The analogies between very small particles of transition metals frequently used in heterogeneous catalysis<sup>1</sup> and molecular clusters, which are more seldom used in homogeneous

catalysis,<sup>2</sup> have been recently examined.<sup>3</sup> Although these two classes of compounds belong to different fields of chemistry, namely, molecular and solid-state chemistry, many comparisons were made possible by the fast development of the synthesis and characterization of new molecular clusters of increasing nuclearity.<sup>4</sup> It appears that geometric as well as

\* To whom correspondence should be addressed at the Institute de Recherche sur la Catalyse.