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Thermodynamic Stability of Gaseous Scandium Silicides and Germanides

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The equilibria involving the gaseous species above the Sc/Si and Sc/Ge alloy systems have been experimentally investigated by high-temperature mass spectrometry. The previously unknown gaseous molecules ScGe and ScSi were identified, and the respective dissociation enthalpies (in kJ mol^{-1}) were evaluated as $D_0^\circ = 266.2 \pm 11$ for ScGe and $D_0^\circ = 223.5 \pm 14$ for ScSi. The corresponding standard heats of formation, $\Delta H^\circ_{f,298}$, are 482 ± 11 and 614 ± 14 kJ mol^{-1}. Also determined were upper limits for the atomization energies of the molecules $ScGe_2$ and $ScSi_2$.

The authors have been engaged for several years in the Knudsen effusion mass-spectrometric determination of the stabilities of molecules containing silicon or germanium[1-6] and various transition metals. The interconnection of the silicon and germanium structures on integrated-circuit chips requires metallization processes which are based on reactions between the metal layer and that of the silicon or germanium. This reaction produces a stable electrical contact by formation of a metal silicide or germanide layer intermediate between the thin layer and the silicon or germanium substrate. The diatomic molecules, the smallest bonding units, potentially contain basic information relative to large clusters of these bimetallic molecules.

The present study has been aimed at the determination of bonding and thermodynamic properties of small intermetallic scandium clusters. Together with the previous similar investigations of the systems yttrium-germanium and yttrium-silicon,[4] these studies present the first experimental data of molecules consisting of an electropositive transition metal and a semiconductor element. The gaseous molecules ScGe and ScSi were shown to exist in the gas phase above their respective alloys. Also observed were the gaseous species Sc, Si, Ge, Ge_2 and Si_2. No polyatomic clusters could be observed. The thermodynamic results for ScGe(g) and ScSi(g) are presented in this paper together with estimated upper values for the molecules $ScGe_2$ and $ScSi_2$. The measured bond energies are discussed in terms of empirical models of bonding with germanium and silicon.

Experimental

A 90° sector, 12 in‡ radius magnetic focusing mass spectrometer (Nuclide, 12-90-HT) equipped with a Knudsen cell assembly was employed in these investigations. The graphite Knudsen effusion cell, used in the first run, had an orifice of 1.0 mm diameter and was charged with a mixture of scandium powder, gold wire, germanium powder and a small amount of silver wire. The latter served as the calibrant. The presence of gold also permitted a redetermination of the dissociation energy of the molecule AuGe[3] and the thermodynamic evaluation of the pressure-independent gas-phase reaction $ScGe + Au \rightleftharpoons AuGe + Sc$.

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‡ 1 in $= 2.54 \times 10^{-2}$ m.

Table 1. Evaluated total intensities (in A) of the pertinent ions observed above the Sc/Ge condensed system and third-law enthalpies for the reaction $ScGe(g) \rightleftharpoons Sc(g) + Ge(g)$[a]

	total ion intensity, I^{+} [b]					
T/K	Ge^{+}	Sc^{+}	$ScGe^{+}$	$\log K_p$	$-\Delta[(G^\circ_T - H^\circ_0)/T]$ /J K^{-1} mol^{-1}	ΔH°_0 /kJ mol^{-1}
1980	2.590 (−07)	2.100 (−09)	4.103 (−12)	1.493	102.5	259.5
2010	2.937 (−07)	2.196 (−09)	3.692 (−12)	1.382	102.6	259.5
1944	8.778 (−08)	1.227 (−09)	1.559 (−12)	1.784	102.3	265.3
1968	1.261 (−07)	1.379 (−09)	1.368 (−12)	1.514	102.4	258.6
2005	1.480 (−07)	2.178 (−09)	2.735 (−12)	1.539	102.6	264.8
1960	6.351 (−08)	1.671 (−09)	1.962 (−12)	1.887	102.4	271.5
2005	7.914 (−08)	1.833 (−09)	1.962 (−12)	1.741	102.6	272.6
2028	1.491 (−07)	3.590 (−09)	5.195 (−12)	1.592	102.7	270.2
2064	1.515 (−07)	5.820 (−09)	5.744 (−12)	1.411	102.9	268.2
2090	8.623 (−08)	6.930 (−09)	3.857 (−12)	1.402	103.1	271.5
					average	266.2 ± 5.2

[a] Numbers in parentheses represent powers of ten. [b] The corresponding partial pressures (in atm) are calculated according to: $P_i = k_i I^{+} T$, using $k_{Ge} = 1.20 \times 10^{-1}$, $k_{Sc} = 5.0 \times 10^{-2}$ and $k_{ScGe} = 4.9 \times 10^{-2}$ atm A^{-1} K^{-1}.

The molecular beam originating from the Knudsen cell was ionized with 16 eV electrons. Other operational conditions were an emission current of 0.30 mA, a filament current of 5.20 A, a 4.5 kV acceleration potential and a 0.08 mA dynode string current. Ionic species observed were Ag^{+}, Ag_2^{+}, Ge^{+}, Ge_2^{+}, Ge_3^{+}, $AuGe^{+}$, Au^{+}, Sc^{+}, $AuSc^{+}$ and $ScGe^{+}$.

In the second run a molybdenum Knudsen cell with an orifice of 0.50 mm diameter was employed and charged with a mixture of scandium and silicon and a small amount of silver, used as the calibrant. The molecular beam was ionized with 18 eV electrons and the ions Ag^{+}, Ag_2^{+}, Si^{+}, Si_2^{+}, Sc^{+} and $ScSi^{+}$ were identified and measured.

All ions were characterized by their mass-to-charge ratios, normal shutter profiles, ionization efficiency and, where possible, their appearance potentials. Owing to the very small ion currents of $ScGe^{+}$ and $ScSi^{+}$, no reliable appearance potentials could be measured for these species. Their identification with the corresponding neutral molecules is, however, not in doubt, because no polyatomic scandium-germanium or scandium-silicon molecules which could have contributed to fragment $ScGe^{+}$ or $ScSi^{+}$, could be observed although a thorough search for them had been made. The measured ion intensities, after being corrected for isotopic abundance, are listed in tables 1 and 2.

At the start of both runs, several data sets of Ag^{+} and Ag_2^{+} were measured at lower temperatures and used to determine the instrumental constant, k_{Ag}, by evaluating the equilibrium reaction $Ag_2(g) \rightleftharpoons 2\,Ag(g)$. The necessary dissociation enthalpy $D^\circ_0(Ag_2) = 172.0 \pm 6.3$ kJ mol^{-1} and Gibbs energy functions were taken from ref. (7). The corresponding k_i values for the other species were calculated by the relationship

$$k_i = k_{Ag}\sigma_{Ag}\gamma_{Ag}E_i/\sigma_i\gamma_i E_{Ag}.$$

The relative maximum atomic ionization cross-sections, σ_i, were taken from ref. (8) for the atoms. The ionization cross-sections for the molecular species were estimated as 0.75 times the sum of the atomic cross-sections.[9] The multiplier gains, γ_i, were experimentally determined for the atomic ions, Ag^{+}, Ge^{+}, Si^{+} and Sc^{+} and estimated for the molecular ions. The factor E_i, which corrects the measured ion intensities to the maximum ionization efficiency, was obtained from the experimental ionization efficiency curves. The $10^{-2}k_i$ values, in atm† A^{-1}K^{-1}, that relate the ion currents to the

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† 1 atm = 101 325 Pa.

Table 2. Evaluated total intensities (in A) of the pertinent ions observed above the Sc/Si condensed system and third-law enthalpies for the reaction $ScSi(g) \rightleftharpoons Sc(g)+Si(g)$ [a]

	total ion intensity, I^{+} [b]					
T/K	Si^{+}	Sc^{+}	$ScSi^{+}$	$\log K_p$	$-\Delta[(G^\circ_T-H^\circ_0)/T]$ /J K^{-1} mol^{-1}	ΔH°_0 /kJ mol^{-1}
1930	1.194 (−08)	1.954 (−07)	2.056 (−13)	0.3893	106.7	220.3
1960	1.980 (−08)	3.698 (−07)	6.014 (−13)	0.3520	106.8	222.5
2008	2.612 (−08)	5.745 (−07)	7.034 (−13)	0.0979	107.0	218.6
2012	2.909 (−08)	5.536 (−07)	4.252 (−13)	0.1522	107.0	209.4
2050	4.049 (−08)	2.773 (−07)	8.211 (−13)	0.2821	107.1	230.7
2082	4.951 (−08)	9.174 (−07)	1.120 (−12)	0.1967	107.2	215.4
2002	1.634 (−08)	2.511 (−07)	3.145 (−13)	0.3128	106.9	226.1
2040	2.123 (−08)	3.300 (−07)	3.145 (−13)	0.0723	107.1	221.3
2059	2.767 (−08)	4.016 (−07)	5.531 (−13)	0.1131	107.1	225.1
2083	4.048 (−08)	4.781 (−07)	9.769 (−13)	0.1138	107.2	227.9
2129	6.825 (−08)	5.606 (−07)	2.115 (−12)	0.1441	107.4	234.5
2115	5.098 (−08)	3.280 (−07)	6.724 (−13)	0.0880	107.3	227.4
2147	8.770 (−08)	4.324 (−07)	1.215 (−12)	0.0964	107.4	226.7
						average 223.5 ± 6.4

[a] Numbers in parentheses represent powers of ten. [b] The corresponding partial pressures (in atm) are calculated according to: $P_i = k_i I^{+} T$, using $k_{Si} = 1.73 \times 10^{-2}$, $k_{Sc} = 5.6 \times 10^{-3}$ and $k_{ScSi} = 5.2 \times 10^{-3}$ atm A^{-1} K^{-1}.

Table 3. Gibbs energy functions, $-(G^\circ_T - H^\circ_0)/T$ (in J K^{-1} mol^{-1}) and heat content functions, $H^\circ_T - H^\circ_0$ (in kJ mol^{-1}) for ScGe and ScSi

		T/K						
		298	1300	1500	1700	1900	2100	2300
ScGe	GEF	218.8	269.4	274.6	279.1	283.1	286.8	290.1
	HCF	9.619	46.67	54.13	61.60	69.08	76.55	84.02
ScSi	GEF	208.1	257.7	262.8	267.3	271.3	274.9	278.2
	HCF	9.378	46.19	53.64	61.10	68.57	76.04	83.51

corresponding partial pressures according to $P_i = k_i I^{+} T$, are for run I: Ag, 11.9 ± 3.9; Ag_2, 7.9 ± 4.0; Ge, 12.0 ± 4.6; Sc, 5.0 ± 2.4 and ScGe, 4.9 ± 2.5. The respective values for run II are Ag, 1.24 ± 0.50; Ag_2, 0.83 ± 0.48; Si, 1.73 ± 0.70; Sc, 0.56 ± 0.31 and ScSi, 0.52 ± 0.30.

Results

Calculation of Thermal Functions

The Gibbs energy functions, $(G^\circ_T - H^\circ_{298}/T)$, and the heat content functions, $H^\circ_T - H^\circ_{298}$, were taken from ref. (10) for the elements Sc(g), Si(g) and Ge(g). Those for the new molecules ScGe(g) and ScSi(g) were calculated by means of standard statistical thermodynamic relations, and are listed in table 3, for 0 K reference temperature.

A bond distance of 25.4 nm was assumed for the molecule ScGe(g). This assumption was made using the sum of the single-bond covalent radii shortened by the same amount as that in AuGe(g).[3] A vibrational frequency of 352 cm^{-1} was evaluated for a harmonic oscillator. The internuclear distance and vibrational frequency of ScSi were estimated as: $r_e = 25.0$ nm and $\omega_e = 446$ cm^{-1}. The stretching force constants of 203 N m^{-1} for ScSi and ScGe were taken as that determined for AuGe.[11] The electronic contribution to the Gibbs energy functions used was 5.763 J K^{-1} mol^{-1}, assuming a ground state with a multiplicity of $g_i = 2$, for both ScGe and ScSi.

Evaluation of the Thermodynamic Properties

The enthalpies for the reactions

$$\mathrm{ScGe(g)} \rightleftharpoons \mathrm{Sc(g)} + \mathrm{Ge(g)} \tag{1}$$

and

$$\mathrm{ScSi(g)} \rightleftharpoons \mathrm{Sc(g)} + \mathrm{Si(g)} \tag{2}$$

have been evaluated by the third-law method according to the relations discussed in literature.[13] The third-law enthalpy change for reaction (1) is $\Delta H^\circ_0 = 266.2 \pm 11$ ($\Delta H^\circ_{298} = 271.0$) kJ mol^{-1} (see table 1). The third-law enthalpy for reaction (2), was obtained as $\Delta H^\circ_0 = 223.5 \pm 14$ ($\Delta H^\circ_{298} = 228.7$) kJ mol^{-1} (see table 2). The uncertainties listed are twice the statistical error computed from data in tables 1 and 2.

For the first run the enthalpies of the reactions

$$\mathrm{AuGe(g)} \rightleftharpoons \mathrm{Au(g)} + \mathrm{Ge(g)} \tag{1a}$$

and

$$\mathrm{AuGe(g)} + \mathrm{Sc(g)} \rightleftharpoons \mathrm{ScGe(g)} + \mathrm{Au(g)} \tag{1b}$$

were also evaluated, yielding for reaction (1*a*) the third-law enthalpy, $\Delta H^\circ_0 = 279.8 \pm 4.5$ kJ mol^{-1} ($\Delta H^\circ_{298} = 283.4$) and the second-law enthalpy, $\Delta H^\circ_{1743} = 287.4 \pm 10.4$ kJ mol^{-1} ($\Delta H^\circ_0 = 273.6$; $\Delta H^\circ_{298} = 277.2$). These were based on 25 data sets measured over the temperature range 1508–2064 K. The necessary thermal functions for AuGe(g) were taken from ref. (3). From these reaction enthalpies an average value of $D^\circ_0 = 276.7 \pm 8$ kJ mol^{-1} or $D^\circ_{298} = 280.3$ kJ mol^{-1} is selected for the dissociation energy of the molecule AuGe. This value is in good agreement with the corresponding literature values: $D^\circ_0(\mathrm{AuGe}) = 270.5 \pm 5.0$ kJ mol^{-1} [3] and $D^\circ_0(\mathrm{AuGe}) = 273.3 \pm 19$ kJ mol^{-1}.[12]

The third-law enthalpy for reaction (1*b*) was obtained as $\Delta H^\circ_0 = 15.7 \pm 6.3$ kJ mol^{-1} ($\Delta H^\circ_{298} = 14.5$), based on 11 data sets measured between 1894 and 2090 K. Combining this enthalpy value with the third-law dissociation energy, $D^\circ_0(\mathrm{AuGe}) = 279.8 \pm 8$ kJ mol^{-1}, from the present investigation yields $D^\circ_0(\mathrm{ScGe}) = 261.1 \pm 14.3$ kJ mol^{-1}, in agreement with the value obtained by direct dissociation. The use of this auxiliary pressure-independent reaction provides a suitable cross-check, because errors in the pressure calibration cancel out.

For the evaluation of an upper limit for the atomization energies of the expected trimers $\mathrm{ScGe_2(g)}$ and $\mathrm{ScSi_2(g)}$, the following gas-phase reactions were considered:

$$\mathrm{ScGe_2(g)} \rightleftharpoons \mathrm{Sc(g)} + 2\mathrm{Ge(g)} \tag{3}$$

$$\mathrm{ScSi_2(g)} \rightleftharpoons \mathrm{Sc(g)} + 2\mathrm{Si(g)}. \tag{4}$$

No shutter effect was observed within the vicinity of the expected m/e for either molecule, at the highest measured temperatures. An estimation of an ion intensity equal to 1.8×10^{-12} A was made for $\mathrm{ScGe_2}$ and 1.6×10^{-12} A for $\mathrm{ScSi_2}$. These intensities represent the minimum shutter effect one could expect to observe at the highest temperatures. The Gibbs energy functions were estimated in an analogous way to those of the corresponding diatomic molecule. A third-law evaluation was performed, yielding an enthalpy of $\Delta H^\circ_0 = 660 \pm 33$ ($\Delta H^\circ_{298} = 667$) kJ mol^{-1} for reaction (3), and $\Delta H^\circ_0 = 678 \pm 32$ ($\Delta H^\circ_{298} = 686$) for reaction (4). These values are upper limits for the atomization energies of these molecules.

Table 4. Comparison of experimental and calculated values of the dissociation energies of diatomic molecules by the atomic-cell model (in kJ mol^{-1})

molecule	D_0° (exptl)	ref.	D_0° (calcd)[a]
ScSi	223	this work	357
ScGe	266	this work	339
YSi	254	4	345
YGe	275	4	329
PdSi	257	18	327
PdGe	252	6	308
NiGe	287	19	296

[a] Ref. (16).

Using the heat of vaporization[10] for the gaseous atoms: Sc ($\Delta H_0^\circ = 376.1 \pm 4.2$, $\Delta H_{298}^\circ = 377.9$ kJ mol^{-1}), Ge ($\Delta H_0^\circ = 371.5 \pm 2.1$, $\Delta H_{298}^\circ = 374.5$ kJ mol^{-1}) and Si ($\Delta H_0^\circ = 451.3 \pm 4.2$, $\Delta H_{298}^\circ = 459.8$ kJ mol^{-1}), the heats of formation of gaseous ScGe and ScSi were evaluated from the measured dissociation energies as:

	$\Delta H_{f,0}^\circ$	$\Delta H_{f,298}^\circ$
ScGe(g)	482 ± 11	482
ScSi(g)	608 ± 14	614

Discussion

Our investigations of the bond energies of diatomic molecules have been guided by various empirical relations or models,[13,14] such as the Pauling correlation for polar single bonds[15] and the atomic-cell model.[16] Our recent experimental work permitted additional testing of the latter model and the recognition of some of its limitations.

In the atomic-cell model, the enthalpy of formation of heteronuclear diatomic molecules relative to the two pure metal dimers has been derived by means of a model description[16] for the interfacial energies, which is similar to that used by Miedema and co-workers[17] for calculating formation enthalpies of alloys and heats of solution in the condensed phase. Our recent experimental results on diatomic molecules[4,6,18,19] that contain a transition metal and a p-block metal or metalloid such as Si and Ge are compared in table 4 with the corresponding values calculated by the atomic cell model.

The atomic-cell model includes besides the attractive ionic term, also present in the Pauling correlation, a repulsive term that accounts for the mismatch of the electron densities of dissimilar atoms, which make up the molecule. This model has been particularly successful for many diatomic transition-metal molecules for which the Pauling correlation has resulted in dissociation energies that are too small. For diatomic molecules between a transition metal and a p-electron element the atomic cell model also includes an attractive 'hybridization term' by analogy with the findings for the corresponding condensed alloys. This contributes *ca.* 85 kJ mol^{-1} to the dissociation energy of gaseous molecules. The applicability of this additional term appears to be justified for NiGe. The present experimental data show that this 'hybridization term' is negligible for combination of a p-electron element with d-electron-deficient transition metals and with palladium.

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References

1 J. E. Kingcade, K. A. Gingerich and U. V. Choudary, *J. Phys. Chem.*, 1978, **82**, 49.
2 K. A. Gingerich, R. Haque and J. E. Kingcade, *Thermochim. Acta*, 1979, **30**, 61.
3 J. E. Kingcade, U. V. Choudary and K. A. Gingerich, *Inorg. Chem.*, 1979, **11**, 3094.
4 J. E. Kingcade and K. A. Gingerich, *J. Chem. Phys.*, 1986, **84**, 4574.
5 J. E. Kingcade and K. A. Gingerich, *Proc. 33rd ASMS Ann. Conf. Mass Spectrometry and Allied Topics*, May, 1985, San Diego, CA, pp. 902-904.
6 I. Shim, J. E. Kingcade and K. A. Gingerich, *J. Chem. Phys.*, 1986, **85**, 6629.
7 J. E. Kingcade Jr, *Ph.D. Dissertation* (Texas A&M University, 1983).
8 J. B. Mann, in *Recent Developments in Mass Spectrometry, Proc. of the International Conference on Mass Spectrometry*, ed. K. Ogata and T. Hayakawa (University of Tokyo Press, Tokyo, 1970), pp. 814-819.
9 J. Drowart and P. Goldfinger, *Angew. Chem., Int. Ed., Engl.*, 1967, **6**, 581.
10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, OH, 1973).
11 R. F. Barrow, W. J. M. Gissane, and D. N. Travis, *Nature* (*London*), 1964, **201**, 603.
12 A. Neckel and G. Sodeck, *Monatsh. Chem.*, 1974, **103**, 367.
13 K. A. Gingerich, *Current Topics in Materials Science*, ed. E. Kaldis (North Holland, Amsterdam, 1980) vol. 6, pp. 345-462.
14 K. A. Gingerich, *Faraday Discuss. Chem. Soc.*, 1980, **14**, 109.
15 L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 3rd ed., 1960), chap. 3.
16 A. R. Miedema and K. A. Gingerich, *J. Phys. B*, 1979, **12**, 2255.
17 A. R. Miedema and P. F. de Chatel, *Proc. Symp. Theory of Alloy Phase Formation*, ed. L. Bennett (Am. Soc. of Metals, New Orleans, 1979), pp. 344-389.
18 I. Shim, J. E. Kingcade and K. A. Gingerich, *Z. Phys. D*, 1987, **7**, 261.
19 I. Shim, J. E. Kingcade and K. A. Gingerich, *J. Chem. Phys.*, 1988, **89**, 3104.

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