Thermochemical Characterization of Seaborgium Compounds in Gas Adsorption Chromatography

B. Eichler,[†] A. Türler,[†] and H. W. Gäggeler*,[†,‡]

Paul Scherrer Institut, 5232 Villigen, Switzerland, and Departement für Chemie und Biochemie, Universität Bern, 3012 Bern, Switzerland

Received: June 2, 1999; In Final Form: August 31, 1999

The chemical characterization of the element seaborgium ($Z = 106$) requires fast experiments such as gas adsorption chromatographic separations in quartz columns with single atoms in a clearly defined chemical state. The maximum separation time for such experiments of only about 10 s is defined by the relatively short half-lives of the currently known longest-lived isotopes ^{265}Sg and ^{266}Sg. To establish optimum experimental parameters, the required thermochemical quantities for chlorides, oxychlorides, and oxides of seaborgium were estimated by extrapolation. On the basis of these results, the stability and volatility of these compounds could be calculated. By use of empirical correlations, the thermochemical constants of the adsorption processes were evaluated and the retention times calculated, taking into account the composition of the reactive carrier gas. The dioxydichloride of seaborgium proved to be the most suitable chemical state regarding its stability, volatility, and retention. Its standard sublimation enthalpy is expected to be between 125 and 144 kJ/mol (larger than that of WO_2Cl_2), resulting in an adsorption enthalpy between −97 and −108 kJ/mol. If the chemistry of seaborgium significantly deviates from the above predicted behavior, then this could be attributed to the possible influence of relativistic effects.

1. Introduction

Investigations of the chemical properties of the transactinides, i.e., elements with atomic numbers of ≥104, can only be performed at the "one-atom-at-a-time level". This strongly hampers chemical studies and, in general, allows us to measure only chromatographic data of species whose most probable chemical composition must be extrapolated.

In general, the chemical characterization of a transactinide element requires the observation of a group-specific chemical reaction, investigation of relative differences of physicochemical properties (e.g., based on retention temperatures of a given species formed by elements of a given group of the periodic table), and if possible, measurement of physicochemical properties (e.g., determination of adsorption enthalpies).

The element seaborgium (Sg, element 106) presently is the heaviest element that is accessible for chemical studies. Sg is a member of group 6 and should exhibit tungsten-like features. Sg can be synthesized in heavy ion reactions such as the complete fusion of ^{22}Ne with ^{248}Cm. After evaporation of four or five neutrons, the isotopes ^{265}Sg and ^{266}Sg are produced.

The decay properties of these two isotopes are the following:[1−3] ^{265}Sg is an α-emitter with energies between 8.69 and 8.94 MeV and a half-life of 7 s; ^{266}Sg is an α-emitter with energies between 8.52 and 8.77 MeV and a half-life of 21 s.

Gas adsorption chromatography experiments with rutherfordium (Rf, element 104)[4] and dubnium (Db, element 105)[5] have successfully been conducted using the *on-l*ine *g*as chromatography *a*pparatus (OLGA).[6] The expected chemical and nuclear decay properties of Sg should allow again a successful use of the OLGA technique. Model experiments with short-lived isotopes of Mo and W with chlorinating, oxygen-containing carrier gases (He with Cl_2 and O_2) were conducted to study the relevant process parameters of a Sg experiment.[7] Later, the optimized conditions were applied for a separation of Sg.[2,8]

In this work, predictions about the stability and adsorption behavior of different Sg species in the system M−Cl−O are made on the basis of extrapolations and empirical correlations. The retention behavior of the relevant species in gas adsorption chromatographic processes was calculated taking into account the composition of the carrier gas. Such data are essential not only for the selection of optimum parameters for a Sg experiment but also for the evaluation of the results. Presently, a full thermodynamic description of the behavior of single atoms or molecules in a gas adsorption chromatographic experiment is not possible because the quantities that characterize the adsorption behavior, e.g., the stability of condensed phases and the stability and bond energies of a molecule on a solid-state surface, cannot be calculated precisely. Therefore, predictions are a necessity in order to obtain crucial information needed for designing a gas chromatographic separation. However, theoretical predictions about (average) bond energies are possible between atoms in the molecules of interest, including relativistic effects, which become increasingly important for the heaviest elements.[9−11] Such calculations yield information about the stability of single molecular states.

Extrapolations down the groups of the periodic table, using empirical correlations, give access to thermodynamic data that is otherwise not available, thereby allowing conclusions about differences between the results of relativistic calculations and results obtained on the basis of continuous trends. Even though the extrapolations are considering possible relativistic effects already manifested in the lighter homologues, they do not include nonlinear effects due to the strong increase of Coulomb forces in the heaviest elements, which are proportional to Z^2.

[†] Paul Scherrer Institut.

[‡] Universität Bern.

10.1021/jp9917751 CCC: $18.00

Hence, such predictions cannot yield information on possible abrupt changes in the chemical properties of the heaviest elements.[12]

2. Relationship between Thermochemical Properties of Macroscopic Phases and the Behavior of Single Molecules of a Compound

The objective of chemically characterizing the properties of an element on the basis of the behavior of only a few atoms requires some explanations about the relationship between macro- and microamounts. The species to be characterized contain radioactive nuclides with known decay properties, which are used for their identification after a chemical separation.

The behavior of a species in a gas adsorption chromatographic experiment is determined by its chemical state and its adsorption properties. The latter is determined not only by the molecular properties of the species but also by the nature of the adsorbing solid-state surface (column material).

The chemical state of single molecules cannot be described on a thermochemical basis. We therefore assume that the stability of a single molecule is proportional to the state function that characterizes the stability of macroscopic phases. The equilibrium constants of formation or adsorption reactions are interpreted as probabilities for the existence of the species in a given chemical state. We assume, by using extreme surpluses of the reaction partners in the reactive carrier gas during the chromatographic process, that for the single molecule the thermochemically most stable state is also reached quickly. In the case of decay processes or secondary reactions, the re-formation of the primary chemical state should take place.

As a measure of the stability of compounds, we examined the standard formation enthalpies of gaseous and solid compounds. On the basis of the so-found empirical relationships between elemental and molecular properties of group 6 elements, properties of Sg compounds were extrapolated and the standard sublimation enthalpies calculated. The sublimation enthalpies were then used as a measure of their volatilities.

Apart from the structure and the stability of gaseous molecules, the volatility is determined by changes in structure and stability during crystallization. The volatility of a compound is mainly defined by the intermolecular forces, which depend on the intramolecular structures and bonds. It is known that strongly ionic compounds that form lattices with high coordination numbers are characterized by a low volatility. Other substances with a low volatility are known to form a network of strong intermolecular interactions through covalent bonds. High volatility is found among compounds with weak intermolecular forces regardless of their nature.

In the transition from the gas phase to the solid state, the molecular structure can remain preserved. Short-range interactions (dipole−dipole, induction, dispersion) between molecules with covalently bound atoms then signify very high volatility. If the coordination of the central atom is not yet saturated, a coordination through nondirectional, partially ionic interactions or the formation of unidirectional, covalent bonds to neighboring molecules takes place. The molecular structure and the number of bonds can then change during the transition from free molecule to crystalline compound. The volatility is therefore determined not only by the ratio of ionic and covalent bonds in the free molecule or by its dipole moment but also by the changes in structure and bonding in the process of condensation and crystallization.

Qualitatively, for adsorption processes the same arguments hold. In the state of zero coverage the energy of adsorption of chlorides or oxychlorides is determined by their molecular properties and the properties of the stationary phase (e.g., chlorinated quartz surface). However, the differences between the adsorption energies of a single chloride or oxychloride molecules of, for example, elements of a given group of the periodic table should be mainly determined by the *relative* volatility sequence of these compounds.

As a measure of the volatility of a compound, we chose the standard sublimation enthalpy to minimize the influence of the various pure solid-phase structures on their volatility. This influence is especially apparent in the entropy of solid phases and may influence the vapor pressure of a compound to a great extent. The concept, that the bond energies between identical molecules in the crystal lattice should be proportional to the adsorptive bond energies between the same, single molecules and a surface, was demonstrated with the empirical correlation found between adsorption enthalpies of single molecules on quartz surfaces and the standard sublimation enthalpies of the respective substances.[13]

Apart from the prediction of the adsorption enthalpy, the prediction about the behavior of single molecules in the gas adsorption chromatographic process requires the calculation of the adsorption entropy and a physicochemical description of the transport of a substance in the chromatographic tube to determine the retention data. This was accomplished on the basis of the theory of ideal linear gas chromatography.[14] The standard adsorption entropy was calculated using the model of mobile adsorption.[15] The chromatographic process can also be described on the basis of a simplified microscopic model about the adsorption−desorption process and the gas-phase transport in a column using a Monte Carlo procedure.[16]

On the basis of stability, volatility, and retention data obtained as described above, optimum parameters for a gas adsorption experiment can be selected. These parameters are composition of the reactive carrier gas, temperature regime, column dimension, and gas flow rate, with the objective of achieving high yields and good separation from interfering nuclides that may disturb detection of the desired species.

3. Methods of Extrapolation and Empirical Correlations

Extrapolations were carried out by taking advantage of thermochemical relationships between elements and their compounds. As reference for the extrapolation of formation enthalpies, the standard enthalpies of the gaseous monatomic elements $\Delta H°(M(g))$ were used. The decision to choose $\Delta H°(g)$ as a starting quantity is based on the consideration that bond energies between different atoms are proportional to the bond energies of homodinuclear bonds. Various authors have modified this Pauling relationship to include reactions with condensed phases. Here, the homodinuclear bond energy is substituted through fractions of the sublimation enthalpy of the elements.[17−19]

An estimate of the errors of the extrapolated results is difficult because of the nature of the considered relationships but principally also because of few (sometimes only two) data points. As a consequence, we define the error of the extrapolated results by establishing a realistic range for the reference quantity $\Delta H°(Sg(g))$.

$\Delta H°(Sg(g)) = 897$ kJ/mol, denoted by Sg I, was estimated on the basis of a correlation of $\Delta H°(M(g))$ (M = Cr, Mo, W) with the atomic number, accounting for possible shell effects.[20] In analogy to a procedure described in refs 21−23, a different extrapolation yielded $\Delta H°(Sg(g)) = 1030$ kJ/mol (denoted by Sg II), using the complex relationships between mole mass, solid-state entropy, mole volume, density, bulk modulus, and sublimation enthalpy. These two values were used as limits for the subsequent extrapolations.

In the next step we determined the atomic formation enthalpies ΔH^* of gaseous and solid $MO_xCl_y(g,s)$ with $\Delta H°(M(g))$ according to

$$\Delta H^*(MO_xCl_y(g)) = \Delta H°_f(MO_xCl_y(g)) - x\Delta H°(O(g)) - y\Delta H°(Cl(g)) - \Delta H°(M(g)) \quad (1)$$

$$\Delta H^*(MO_xCl_y(s)) = \Delta H°_f(MO_xCl_y(s)) - x\Delta H°(O(g)) - y\Delta H°(Cl(g)) - \Delta H°(M(g)) \quad (2)$$

with

$$\Delta H°_f = \text{standard formation enthalpy}$$

$$\Delta H°(O,Cl,M) = \text{standard enthalpy of monatomic gaseous elements}$$

For Sg, $\Delta H^*(MO_xCl_y(g,s))$ was extrapolated from $\Delta H°(M(g))$ as described below. With the quantities ΔH^*, the standard sublimation enthalpies may be inferred from

$$\Delta H°_{subl} = \Delta H^*(MO_xCl_y(g)) - \Delta H^*(MO_xCl_y(s)) \quad (3)$$

or dissociation enthalpies of the reaction $MO_xCl_y(g) \Leftrightarrow MO_xCl_{y-1}(g) + Cl(g)$ may be inferred from

$$\Delta H_{diss} = \Delta H^*(MO_xCl_{y-1}(g)) - \Delta H^*(MO_xCl_y(g)) \quad (4)$$

or enthalpies of the substitution reactions $MCl_x(g) + O(g) \Leftrightarrow MOCl_{x-2}(g) + 2Cl(g)$ may be inferred from

$$\Delta H_{subst} \Leftrightarrow \Delta H°_f(MOCl_{x-2}(g)) + 2\Delta H°(Cl(g)) - \Delta H°_f(MCl_x(g)) - \Delta H°(O(g))$$

$$\Delta H_{subst} \Leftrightarrow \Delta H^*(MOCl_{x-2}(g)) - \Delta H^*(MCl_x(g)) \quad (5)$$

In a correlation of $\Delta H^*(MO_xCl_z)$ against $\Delta H°(M(g))$ for elements of a given group, the stability of the compound MO_xCl_z increases with increasing atomic number if the slope of the correlation line is greater than 1. This is caused by the fact that in the quantities $\Delta H^*(MO_xCl_z)$ the $\Delta H°(M(g))$ values of the metals are already included. This limiting condition is not valid for the trends of sublimation, dissociation, and substitution enthalpies for the compounds of the elements of a given group as a function of $\Delta H°(M(g))$.

The entropy values of gaseous compounds are needed to investigate gas-phase transport reactions. As discussed in section 5.7, the entropies of the solid state influence the vapor pressure equilibrium. Entropies may be extrapolated via their relationship to the mole mass *m* of the compound X for elements of a given group (version I).

$$S°(X(g)) = a \ln(m) + b \quad (6)$$

A second approximation is obtained[33] by subtracting the entropy of the metals from the entropy of isomolecular compounds and adding the average of the difference to the entropy of Sg ($S°(Sg(g)) = 178.3$ J mol^{-1} K^{-1})[21] (version II).

Finally, a third approximation is based on the entropy differences of the tungsten compounds only (version III).

4. Results of the Extrapolations

4.1. Stability and Volatility of Chlorides. The atomic formation enthalpies of the chlorides of group 6 elements were calculated on the basis of tabulated data[24−28] with eqs 1 and 2 and are depicted in parts a and b of Figure 1 as a function of the standard enthalpy of the gaseous metals. The straight lines are linear regressions. The slopes are generally positive but mostly smaller than 1. Only for the hexachlorides is the slope greater than 1, indicating an increasing stability from $MoCl_6$ to WCl_6. The results of the extrapolation, including the standard sublimation enthalpies calculated with eq 3, are summarized in Table 1.

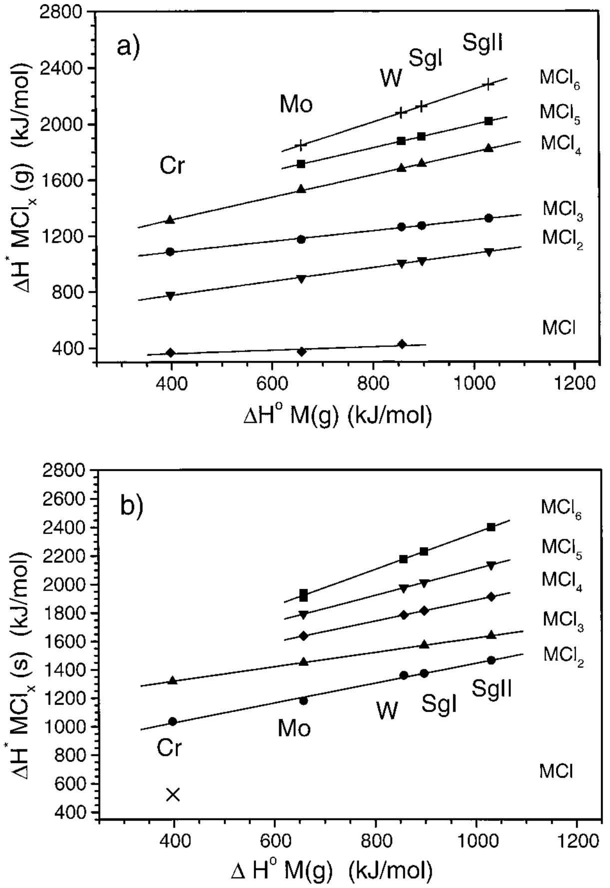

Figure 1. Atomic formation enthalpies of the gaseous (a) and solid (b) chlorides of the group 6 elements as a function of the standard enthalpies of the gaseous metals.

TABLE 1: Extrapolated Atomic Formation Enthalpies of the Chlorides, Oxychlorides, and Oxides of Sg and Their Standard Sublimation Enthalpies (in kJ mol^{-1})

	Sg I			Sg II		
compound	$-\Delta H^*(s)$	$-\Delta H^*(g)$	ΔH_{subl}	$-\Delta H^*(s)$	$-\Delta H^*(g)$	ΔH_{subl}
$SgCl_2$	1373	1020	353	1466	1085	380
$SgCl_3$	1571	1272	300	1639	1322	317
$SgCl_4$	1815	1714	101	1913	1820	93
$SgCl_5$	2013	1908	105	2137	2018	119
$SgCl_6$	2230	2125	105	2400	2279	121
$SgOCl_4$	2413	2318	95	2612	2504	108
SgO_2Cl_2	2492	2367	125	2695	2551	144
SgO		683			755.3	
SgO_2	1986	1330	657	2122	1438	684
SgO_3	2517	1967	549	2727	2108	619

In Figure 2a, the standard sublimation enthalpies of the group 6 chlorides, including the extrapolated results for Sg, are shown as a function of the standard enthalpies of the gaseous metals.

The extrapolated thermochemical data for the oxidation states of ≤3 are only approximate values because of uncertainties in the literature data. Certainly, $SgCl_2$ and $SgCl_3$ are relatively low-

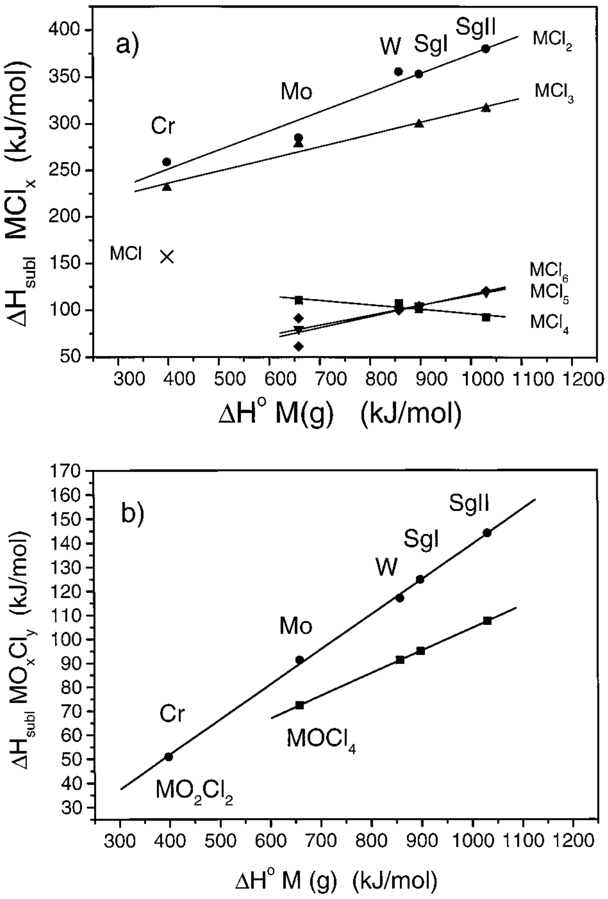

Figure 2. Standard sublimation enthalpies of the chlorides (a) and oxychlorides (b) of the group 6 elements as a function of the standard enthalpies of the gaseous metals.

volatile compounds tending to thermal decomposition (in fictive, macroscopic systems they would tend to disproportionate).

The compounds suitable for gas adsorption chromatographic experiments are the tetra-, penta-, and hexachlorides because of their relatively low sublimation enthalpies. The volatilities of $SgCl_5$ and $SgCl_6$ are almost identical. They are similarly or a little less volatile compared to WCl_5 and WCl_6 but less volatile than $MoCl_5$ and $MoCl_6$.

According to the presented data the volatility sequence is reversed for the tetrachlorides.

4.2. Stability and Volatility of Oxychlorides. Starting from tabulated thermochemical data for the oxytetrachlorides and dioxydichlorides,[24,29−31] the atomic formation enthalpies of the gaseous and solid oxychlorides were calculated and shown in Figure 3 as a function of $\Delta H^\circ(M(g))$. For all compounds the slopes are clearly greater than 1. Therefore, the stability of these compounds increases with Z within the group. The atomic formation enthalpies of the oxychlorides of group 6 elements clearly exceed those of the pure chlorides in the same oxidation state (see Figures 1a,b and 3). The standard sublimation enthalpies for the above-mentioned Sg compounds are summarized in Table 1.

Compared to the homologous W compounds, slightly lower volatilities are to be expected for $SgOCl_4$ and SgO_2Cl_2 (Figure 2b).

A remarkable fact is that the vapor pressure of WO_2Cl_2 is higher than that of $WOCl_4$, even though for the standard sublimation enthalpies the opposite is true. The reason lies in the strongly structure-dependent solid-state entropies of these two compounds. These modify, through the sublimation entropy, the sequence in vapor pressure (see also section 5.7). For the reasons explained in section 2, we maintain the standard sublimation enthalpies as a measure of the volatility and expect for the Sg compounds a decreasing volatility in the sequence $SgOCl_4$ and SgO_2Cl_2.

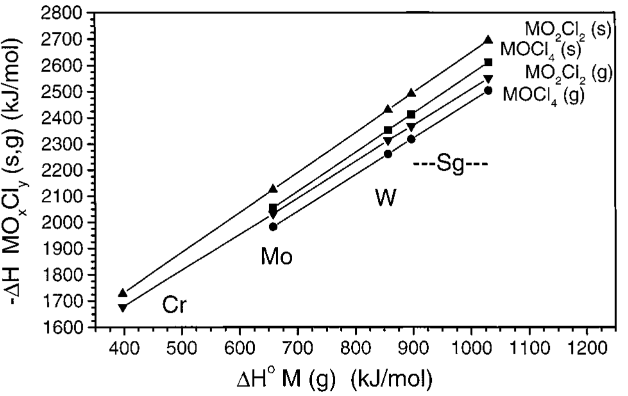

Figure 3. Atomic formation enthalpies of the gaseous and solid oxychlorides of the group 6 elements as a function of the standard enthalpies of the gaseous metals.

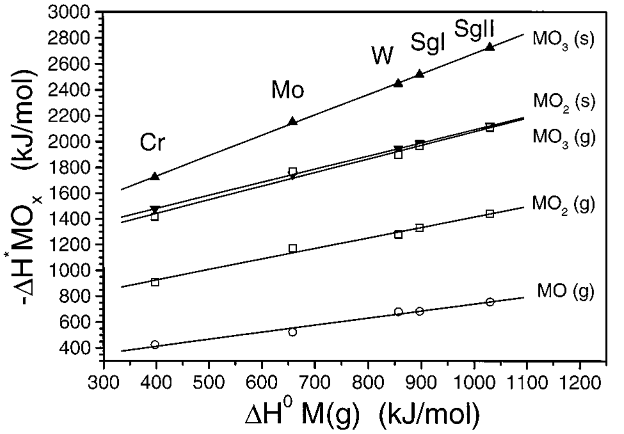

Figure 4. Atomic formation enthalpies of the gaseous and solid oxides of group 6 elements as a function of the standard enthalpy of the gaseous metals.

4.3. Stability and Volatility of Oxides. As decay products of oxychlorides or as initial chemical states of Sg, pure oxides are also possible. Atomic formation enthalpies of the oxides were calculated and plotted in Figure 4 as a function of the standard enthalpies of the metals. The differences represent again the standard sublimation enthalpies. The extrapolated values for Sg compounds are tabulated in Table 1. The stability of solid dioxides and trioxides, as well as the stability of gaseous trioxides, increases with Z within group 6.

In contrast, the stability of the gaseous dioxides and monoxides decreases. Because of their low volatility, the oxides are less suited for gas adsorption chromatographic experiments.[32] However, depending on the reactive carrier gas used, they can coexist with the oxychlorides, which is the reason that the data about the oxides are also relevant for experiments with chlorinating gases.

In this work the sublimation enthalpies always relate to the monomolecular state. Usually, trioxymolecules are associated with polynuclear compounds, which are considerably more volatile but cannot be formed in the carrier-free state.

4.4. Extrapolation of the Entropies of the Solid and Gaseous Compounds. Entropies of the gaseous compounds were extrapolated using literature data.[24,29,31,34,35] The results are shown in Table 2. The entropies of the oxides, chlorides,

TABLE 2: Entropies of Gaseous Compounds of Seaborgium

	$S°(g)$, J mol^{-1} K^{-1}				
compound	version I, eq 6	version II	version III	selection	best value
$SgCl_5$	411	402	424	average	412
$SgCl_6$	419	420	424	version I	419
$SgOCl_4$	375	379	381	average	378
SgO_2Cl_2	364	344	358	version I	364
SgO_3	296	279	289	version I	296

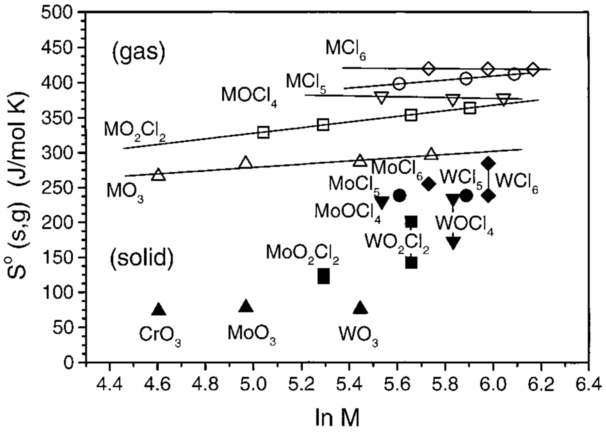

Figure 5. Entropies of the gaseous and solid chlorides, oxychlorides, and oxides of the group 6 elements as a function of the natural logarithm of the mole masses. Data for gaseous compounds are connected straight lines with points for Mo, W, and Sg (from left to right) on the MCl_6, MCl_5, and $MOCl_4$ lines, and for Cr, Mo, W, and Sg on the MO_2Cl_2 and MO_3 lines. No attempt is made to connect the data points for solid compounds. Vertical solid lines connect differing data for the same compound.

and oxychlorides of the group 6 elements, together with the extrapolated values for gaseous seaborgium compounds, are depicted in Figure 5 as a function of the natural logarithm of the mol mass.

The entropies of homologous, gaseous compounds show a continuous, linear behavior with small variations of the entropy values, whereas for the entropy values for the solid phases deviating literature data were found for a given compound, which did not allow simple extrapolations.

5. Discussion of the Extrapolations

5.1. Comparison of Stability and Volatility of the Various Types of Compounds. In Figure 6 the atomic formation enthalpies of solid and gaseous hexachlorides, oxytetrachlorides, dioxydichlorides, and the trioxides of Sg are shown. The compilation permits a comparison of the stabilities and volatilities of the various types of compounds and demonstrates the influence of possible errors in the extrapolation of $\Delta H°(Sg(g))$. The stabilizing effect of oxygen in the transition from the hexachloride to the oxytetrachloride is clearly visible. The highest volatility, i.e., the smallest difference $\Delta H^*(g) - \Delta H^*(s)$, is expected for the oxytetrachloride. For the trioxide a severe break in the trend is observed. While the formation enthalpy of the solid state is monotonically increasing, that of the gaseous trioxide is strongly decreasing.

The already mentioned distinct tendency of gaseous trioxides to polymerize points to strong intermolecular forces, which are manifested in a large adsorption enthalpy of the single molecules[32,36] and which are capable of modifying the gas chromatographic process.

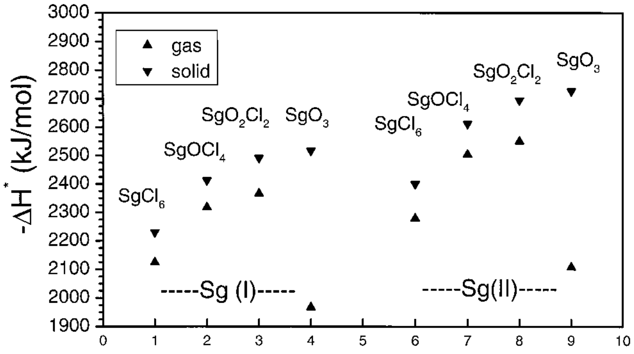

Figure 6. Atomic formation enthalpies of solid and gaseous hexachlorides, oxytetrachlorides, dioxydichlorides, and the trioxides of seaborgium.

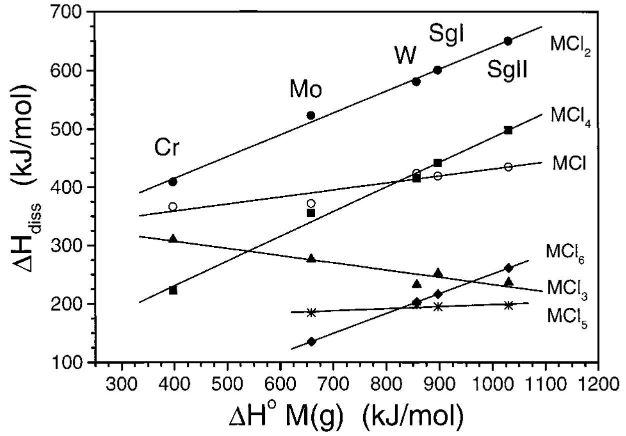

Figure 7. Dissociation enthalpies of the gaseous chlorides as a function of the standard enthalpies of the gaseous metals.

TABLE 3: Dissociation Enthalpies of the Gaseous Sg Chlorides (in kJ mol^{-1})

	dissociation enthalpy	
dissociation step	Sg I	Sg II
hexa–penta	217	262
penta–tetra	195	197
tetra–tri	442	498
tri–di	252	237
di–mono	601	650
mono–metal	419	436
total	2126	2280

5.2. Dissociation Enthalpies of Chlorides. The concept of the stability of a compound or molecule is always to be seen in relation to a second state, considering possible reaction channels to that state. This requires a close examination of the bond energies in the various chemical states and processes in the system M–Cl–O. With eq 4 and ΔH^* of gaseous chlorides in the various oxidation states the dissociation enthalpies were calculated and are shown in Figure 7 as a function of $\Delta H°(M(g))$. The sum of all dissociation enthalpies for each oxidation state is equal to $-\Delta H^*$ of the chloride in the highest oxidation state. The steep increase of the dissociation enthalpies of the tetrachlorides is remarkable, a sign of a stronger increase of the stability within group 6 elements compared to those of the tri- and pentachlorides.

From the extrapolated results compiled in Table 1, the dissociation enthalpies of the Sg chlorides were calculated and are summarized in Table 3. Indications of a relative stability of the oxidation state +4 already existed earlier.[37]

TABLE 4: Dissociation Enthalpies and Average Bond Energies (E_B) of Chlorine in the Chloride Molecules of Group 6 (in kJ mol^{-1})

M	Cr	Mo	W	Sg I	Sg II
ΔH(M(g))	398	659	857	897	1030
MCl					
E_B	−367	−372	−424	−419	−435
$-\Delta H_{diss}$	367	372	424	419	435
MCl_2					
E_B	−388	−448	−502	−510	−542
$-\Delta H_{diss}$	409	523	581	601	650
MCl_3					
E_B	−362	−391	−421	−424	−441
$-\Delta H_{diss}$	310	277	233	252	237
MCl_4					
E_B	−327	−382	−420	−428	−455
$-\Delta H_{diss}$	223	356	416	442	498
MCl_5					
E_B		−342	−375	−382	−404
$-\Delta H_{diss}$		185	198	195	197
MCl_6					
E_B		−308	−346	−354	−380
$-\Delta H_{diss}$		135	202	217	262

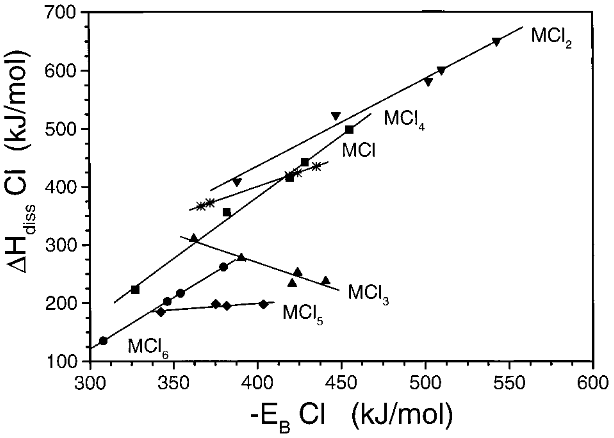

Figure 8. Comparison of the average bond energies with the dissociation enthalpies of the gaseous chlorides.

TABLE 5: Extrapolations of the Bond Energies of Cl and O in the Oxychlorides of Group 6 Elements (in kJ mol^{-1})

		average bond energies	
compound	version	O	Cl
$MoOCl_4$	I	455	382
	II	521	365
	average	488	374
$WOCl_4$	I	583	420
	II	679	396
	average	631	407
$SgOCl_4$ (Sg I)	I	604	428
	II	683	409
	average	644	419
$SgOCl_4$ (Sg II)	I	684	455
	II	755	437
	average	720	446
CrO_2Cl_2	I	450	388
	II	454	385
	average	452	386
MoO_2Cl_2	I	569	448
	II	585	431
	average	577	4394
WO_2Cl_2	I	6556	502
	II	639	518
	average	647	510
SgO_2Cl_2 (Sg I)	I	674	510
	II	665	519
	average	669	514
SgO_2Cl_2 (Sg II)	I	733	543
	II	719	556
	average	726	550

5.3. Comparison of the Average Bond Energies M−Cl with the Dissociation Enthalpies of Chlorides. The average bond energy of a chlorine atom in an isolated chloride molecule MCl_x is defined through $\Delta H^*(MCl_x/x)$.

The dissociation enthalpy ΔH_{diss} is the reaction enthalpy of the process

$$MCl_x(g) \rightarrow MCl_{x-1}(g) + Cl(g) \qquad (7)$$

The systematic analysis of the dissociation enthalpies (Table 4) allows a more reliable assessment of the stability of compounds in each oxidation state than the analysis of average bond energies. Figure 8 shows correlations between the dissociation enthalpies and the average bond energies of gaseous chlorides. The enthalpies of stepwise dissociation show a distinct structure that is much clearer than that of the average bond energies. For particularly stable chlorides the dissociation enthalpy reaches or even exceeds the average bond energy. Increasing stability within group 6 elements is expected for the mono-, di-, tetra-, and hexachlorides.

The trichlorides (decreasing) and pentachlorides (constant) of group 6 elements probably tend to disintegrate if they cannot be stabilized by, for example, the formation of dimers or the formation of heterodinuclear compounds with other chlorides.

5.4. Extrapolation of Bond Energies of Cl and O for Oxychlorides of Group 6 Elements. In the case of asymmetric compounds the dissociation energies are primarily dependent on the sequence of dissociation steps. For the compounds of type $MOCl_4$ and MO_2Cl_2 we observe two limiting dissociation steps:

$$MOCl_4 \rightarrow MCl_4 + O \qquad (8)$$

$$MOCl_4 \rightarrow MO + 4Cl \qquad (9)$$

or

$$MO_2Cl_2 \rightarrow MCl_2 + 2O \qquad (10)$$

$$MO_2Cl_2 \rightarrow MO_2 + 2Cl \qquad (11)$$

In the first step the dissociation enthalpy of the M−O bond is calculated as the difference of the atomic formation enthalpies of $MOCl_4$ and MCl_4 (version I). The average bond energy of the M−Cl bond is then the atomic formation enthalpy of MCl_4 divided by the number of ligands (4).

Alternatively, the average bond energy of the M−Cl bond can be calculated as the difference of the atomic formation enthalpies of $MOCl_4$ and MO divided by the number of Cl ligands (version II). The dissociation enthalpy of the M−O bond is approximated by the atomic formation enthalpy of MO.

The same procedure was applied for the dioxydichlorides, accounting for the different stoechiometry. However, the required data for an analysis of the stepwise dissociation, analogous to the chlorides, are not available.

Table 5 and Figure 9 clearly show that the contribution of the average bond energy of oxygen in the dioxydichlorides increases faster with Z or with $\Delta H°$(M(g)) than that of chlorine. This is also apparent from the analysis of the substitution reactions (section 5.5). In the case of the oxytetrachlorides, the contribution of oxygen to the total bond energy increases even more steeply. This corresponds to the strongly covalent character

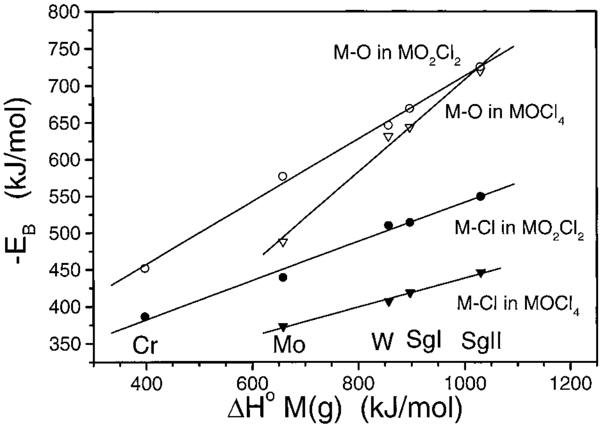

Figure 9. Bond energies of Cl and O in the gaseous oxychlorides of Cr, Mo, W, and Sg as a function of the standard enthalpies of the gaseous metals.

TABLE 6: Enthalpies of the Substitution and Oxidation Reactions of Gaseous Sg Species with Atomic Oxygen (in kJ mol^{-1})

no.	reaction	ΔH_{subst}(Sg I)	ΔH_{subst}(Sg II)
1	$SgCl_6 + O \leftrightarrow SgOCl_4 + 2\ Cl$	−193	−225
2	$SgCl_5 + O \leftrightarrow SgOCl_4 + Cl$	−409	−487
3	$SgCl_4 + O \leftrightarrow SgOCl_4$	−604	−684
4	$SgCl_6 + 2O \leftrightarrow SgO_2Cl_2 + 4\ Cl$	−242	−271
5	$SgOCl_4 + O \leftrightarrow SgO_2Cl_2 + 2\ Cl$	−49	−46
6	$SgO_2Cl_2 + O \leftrightarrow SgO_3 + 2Cl$	+400	+443

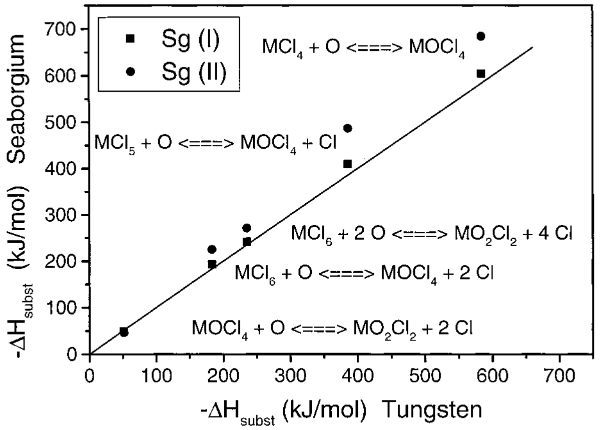

Figure 10. Comparison of the reaction enthalpies of the gaseous chlorides and oxychlorides of Sg with oxygen. The solid line corresponds to $\Delta H_{subst}(Sg) = \Delta H_{subst}(W)$.

of the bonding in these compounds, which is also apparent in the structure and the volatility of the macroscopic phases.

5.5. Enthalpies of Substitution or Oxidation Reactions in Chlorides and Oxychlorides with Oxygen. The thermochemistry of the substitution or oxidation reactions of gaseous species is of interest to evaluate the relative stability of single chemical states in the system M−O−Cl. With eq 5 and the extrapolated results for compounds of seaborgium, the reaction enthalpies for the types of reactions tabulated in Table 6 were calculated.

Reactions 1−5 are exothermic. According to the stability of the single species in the system Sg−Cl−O, the oxidation state +6 should prevail. The dioxydichloride of Sg is to be considered as the most stable state.

Figure 10 shows a comparison of the reaction enthalpies of substitution or oxidation of the chlorides and oxychlorides of Sg and W. Reactions 1−4 from Table 6 are more favored for Sg than the analogous reactions of W. Compared to W, the substitution reaction 5 is less favored for Sg but still exothermic. In an experiment, the small reaction enthalpy requires a careful choice of the composition of the reactive carrier gas to further support the reaction.

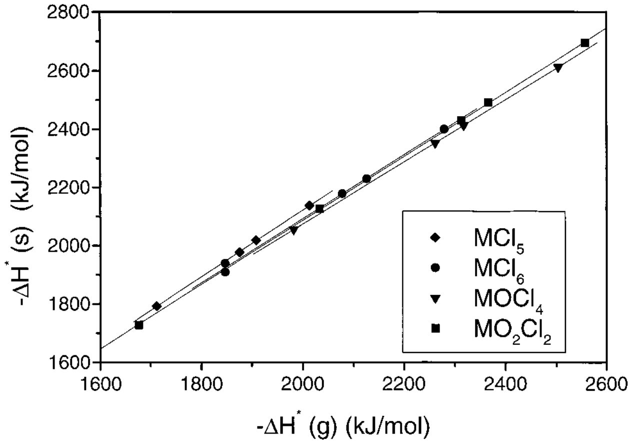

Figure 11. Comparison of the atomic formation enthalpies of solid and gaseous chlorides an oxychlorides of the group 6 elements. Data for compounds are connected by straight lines with points for Mo, W, and Sg (from left to right) on the MCl_6, MCl_5, and $MOCl_4$ lines, and for Cr, Mo, W, and Sg on the MO_2Cl_2 line.

TABLE 7: Constants of the Linear Regression Analysis between Atomic Formation Enthalpies of Solid and Gaseous Chlorides and Oxychlorides

elements	compounds	*a*	*b*
Mo, W	MCl_6	1.1053	−118.8
Mo, W	$MOCl_4$	1.0674	−61.3
Cr, Mo, W	MO_2Cl_2	1.1045	−122.6

5.6. Relationship between the Formation Enthalpies of Solid and Gaseous Chlorides and Oxychlorides. The prediction of chemical properties has to rely on theoretical models or at least empirical relationships between the different properties. However, any extrapolated result needs to be examined. In the following it is discussed whether the extrapolated atomic formation enthalpies of chlorides and oxychlorides fulfill the relationship

$$-\Delta H^*(s) = a[-\Delta H^*(g)] + b \qquad (12)$$

These relationships are shown for the pure chlorides and oxychlorides in Figure 11. The constants *a* and *b* are compiled in Table 7.

The slopes (*a*) of the linear correlations are larger than 1. This means that the stability of the solid phases increases faster than those of the gaseous molecules, leading to the conclusion that with increasing Z the volatility decreases. This shows that generally large (negative) formation enthalpies of the gaseous molecules correlate with high intermolecular forces (low volatility) and small atomic formation enthalpies with low intermolecular interaction (high volatility). Within group 6 the volatility of the dioxydichlorides decreases faster than the volatility of the oxytetrachlorides.

When the atomic formation enthalpies of a chloride or an oxychloride molecule from eq 12 are known, the following relationship allows an estimate of the sublimation enthalpies:

$$\Delta H^*(g) = \frac{\Delta H_{subl} - b}{1 - a} \qquad (13)$$

Conversely, this relationship signifies an important interface for the interpretation of experimental results. With eq 13, the standard sublimation enthalpies are in good agreement with the data derived in sections 4.1 and 4.2.

5.7. Molecule and Crystal Structure of the Chlorides, Oxychlorides, and Oxides of the Group 6 Elements and Their Influence on the Volatility. As noted in section 3, volatility properties are determined by both the structure and bonding within the free molecules, as well as the structure and bonding within the crystalline phase. The respective changes in structure and bonding during crystallization determine the volatility. Therefore, and in order to reach analogous conclusions about the corresponding properties of Sg compounds, these changes are more closely examined.

In the oxygen-containing compounds, $MOCl_4$, MO_2Cl_2, and MO_3, the most serious intramolecular change in the process of forming a crystalline phase is the breakup of oxygen double bonds and the formation of oxygen-bridging bonds between the metal atoms. This process is accompanied by changes in bond length.[9−11,39,43] The composition certainly also influences the bond length.

As a free molecule, $MOCl_4$ has the form of a square pyramid with four Cl atoms in the base[39] ($WOCl_4$: α-UF_5 structure) with a high fraction of covalently bound oxygen (M═O) (see Figure 9 and Table 5). In the solid state the double bond to oxygen is broken and the oxygen becomes a bridging atom between neighboring M atoms. This way octahedral chain structures are formed. At the same time the coordination number changes from 5 to 6. Again, the chains are only held together by van der Waal's forces. Thermochemically, this structural effect requires a high value of the solid-phase entropy, resulting in a relative lowering of the standard sublimation entropy and, therefore, of the vapor pressure.

Entirely different changes in the bonding take place with the inclusion of tetrahedral MO_2Cl_2 molecules in the crystalline lattice. The central atom is then octagonally surrounded by two chlorine atoms and four oxygen atoms in the equatorial plane with asymmetric bond lengths (WO_2Cl_2: quasi SnF_4 structure). The process involves a change from coordination number 4 to 6 on the central atom. The MO_4Cl_2 octahedrons are bridging with two oxygen atoms at the edge to neighboring M atoms. While within the layers ionic and covalent bond fractions are present, between the layers only weak short-range forces exist.

In the case of $MoOCl_4$, the structure-based decrease of the standard sublimation entropy obviously results in a reduced vapor pressure below the one of MO_2Cl_2, even though its standard sublimation enthalpy is smaller than the one of MoO_2Cl_2.

In $WOCl_4$ the decrease of the standard sublimation entropy is not sufficient to change the sequence in vapor pressure,[7] which is due to stronger long-range ionic interactions.

The octahedral WCl_6 molecule changes into a lattice, exhibiting the typical features of a coordination lattice. The volatility does not correspond to the expected loose intermolecular bonds of preexisting WCl_6 octahedral molecules. The entropy of the crystalline phase is high enough that again a considerable decrease of the standard sublimation entropy occurs, which causes a relative reduction of the vapor pressure. For compounds of Sg, similar molecular and crystal structures, as for the lighter homologous W compounds, are expected.

The sequence of vapor pressures in the region of small absolute pressures corresponds to $MoO_2Cl_2 > MoOCl_4 > WOCl_4 > WCl_6 > WO_2Cl_2$.[7] The sequence of standard sublimation enthalpies is different: $MoOCl_4 < MoCl_6 < WCl_6 < WOCl_4 < MoO_2Cl_2 < WO_2Cl_2$. This sequence shows the growing tendency to form a coordination lattice with stronger ionic bonding. The extrapolated standard sublimation enthalpies of Sg compounds suggest that Sg always forms the least volatile compounds of a homologous series in group 6, i.e., $WCl_6 < SgCl_6$, $MoOCl_4 < WOCl_4 < SgOCl_4$, and $CrO_2Cl2 < MoO_2Cl_2 < WO_2Cl2 < SgO_2Cl_2$.

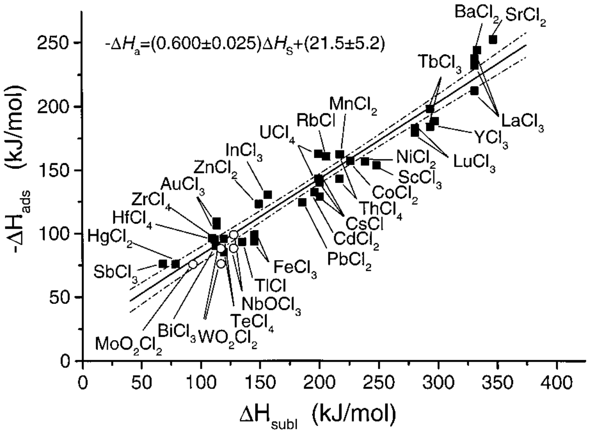

Figure 12. Correlation between the sublimation enthalpy of chlorides and oxychlorides with the corresponding adsorption enthalpy of single molecules on quartz surface.

The changes in the sequence of vapor pressures can be explained by the solid-phase entropies as shown in Figure 5. While the gas-phase entropies are steadily increasing with the natural logarithm of the mole masses, almost independently of their composition, the solid-phase entropies are heavily fluctuating, depending on their individual structural properties. Therefore, the standard sublimation entropies are modified and, accordingly, the vapor pressures are given by

$$\ln p = \frac{-\Delta H_{\mathrm{subl}}}{RT} + \frac{\Delta S_{\mathrm{subl}}}{R} \qquad (14)$$

Because of the large spread in the data of sublimation entropies, we restrict ourselves to a qualitative interpretation and give only a prediction of the standard sublimation enthalpies as a measure of volatility (the arguments have been given in section 2).

6. Gas Adsorption Chromatography as a Tool To Determine Thermochemical Properties

Comparisons between standard sublimation enthalpies (as a measure of volatility) and the adsorption enthalpies of carrier-free species (i.e., zero coverage) for given molecules (e.g., chlorides, oxychlorides, or oxides) showed that there exist good linear correlations[13,36] between these two quantities (see Figure 12).

To calculate adsorption enthalpies, the adsorption entropy has to be known. In contrast to previous work[13,36] where an average adsorption entropy of −167.32 J mol^{-1} K^{-1} was used for chlorides and oxychlorides, the adsorption entropy was calculated individually for each compound as a function of the mole mass and the deposition temperature:[15]

$$\Delta S = R\left\{[\ln(2.2 \times 10^{-13})]\left(\frac{RT}{2\pi M}\right)^{1/2} + \frac{1}{2}\right\} \qquad (15)$$

As a result, the following correlation resulted in 32 different chlorides and oxychlorides:

$$-\Delta H_{\mathrm{ads}} = (0.600 \pm 0.025)\Delta H^{\circ}_{\mathrm{subl}} + (21.6 \pm 5.2) \qquad (16)$$

with a correlation coefficient $R = 0.966$.

TABLE 8: Adsorption Enthalpies and Entropies of Seaborgium Compounds on a Quartz Surface (Calculated Values with ΔH_{subl} from Table 1)

compound	$-\Delta H_{ads}$, kJ mol^{-1} Sg I	Sg II	ΔS_{ads}, J mol^{-1} K^{-1}
$SgCl_5$	85 ± 8	93 ± 8	−168.75
$SgCl_6$	85 ± 8	94 ± 8	−169.07
$SgOCl_4$	79 ± 8	86 ± 8	−168.56
SgO_2Cl_2	97 ± 9	108 ± 9	−167.99
SgO_3	396 ± 30	444 ± 33	−167.32

TABLE 9: Calculated Retention Times (in s) of Several Seaborgium Compounds for the Following Model Assumptions: Column Length = 2 m, $\varnothing = 0.017\,66$ cm^2, Gas Flow Rate $v_0 = 20$ cm^3 s^{-1}, $T = 573$ K, $a/v = 26.667$ cm^{-1}

compound	*t* Sg I	Sg II
$SgCl_5$	0.26	1.14
$SgCl_6$	0.25	1.31
$SgOCl_4$	0.14	0.34
SgO_2Cl_2	2.34	26.67
SgO_3	5.04×10^{27}	1.21×10^{32}

In analogy, a linear correlation of the adsorption enthalpies with the standard sublimation enthalpies was also obtained for the oxides:[36]

$$-\Delta H_{ads} = (0.69 \pm 0.04)\Delta H^{\circ}_{subl} + (16.9 \pm 8.2) \quad (17)$$

Table 8 summarizes predicted adsorption entropies (eq 15) and enthalpies of seaborgium chlorides, oxychlorides, and oxides using eqs 16 and 17 for the two standard enthalpies of Sg(g) (see above).

Adsorption enthalpy values can now be used to predict retention times *t* (s) of a substance in an isothermal chromatographic process, which can be described by[14,40−42]

$$t(T) = L\left(\frac{T\varnothing}{v_0 T}\right)\left(1 + \frac{aVf_c}{vA}\exp\left(\frac{-\Delta H_{ads}}{RT}\right)\exp\left(\frac{\Delta S_{ads}}{R}\right)\right) \quad (18)$$

with *L* being the column length, v_0 the gas flow, $\varnothing$ the open column cross section, *T* the temperature, a/v the relation of the inner surface to empty column volume, V/A the relation of standard mole volume to standard mole surface (1 cm), *R* the gas constant (8.314 J mol^{-1} K^{-1}), T_0 the standard temperature (273 K), and factor $f_c = 1$ if chromatography occurs without surface chemical reactions.

If a chemical reaction is superimposed, f_c depends on the composition of the reactive carrier gas.[41,42] As an example, by use of eq 18, the retention times in a typical chromatographic column for the seaborgium compounds from Table 8 are summarized in Table 9.

Dissociative or substitutive adsorption reactions are possible competing processes to the chromatography of molecules without chemical interaction. In the following, thermochemical predictions are made for some possible heterogeneous reactions on the quartz surface. For these predictions the standard formation enthalpies (as deduced from the atomic formation enthalpies of the gaseous compounds), the enthalpies and entropies of the adsorption reactions, and the entropies of the gaseous compounds, including $S^{\circ}(Cl(g))$ and $S^{\circ}(O_2(g))$, were used[39] to calculate the thermochemical data and equilibrium constants of the gas-phase reactions and the complex adsorption processes.

To determine the most probable chemical species, it is necessary to analyze the influence of the temperature and composition of the reactive carrier gas. From the predicted adsorption enthalpies (Table 8) it follows that, for technical reasons, the volatile chlorides and oxychlorides are best suited. However, the adsorption enthalpies of the penta-, hexa-, and oxytetrachlorides are very similar, which makes the determination of the species on the basis of experimental retention data impossible. An analysis of the thermochemical data of the atomic substitution reactions (Table 6) and the gas-phase reactions (standard state) (Table 10) shows that the formation of oxychlorides in the reaction of the pure chlorides with oxygen is a thermodynamically favorable process. However, the reaction of the dioxydichloride with oxygen to the trioxide is not likely. Since oxygen is always present in real experiments in trace amounts, the preferential choice is the oxychlorides as the most

TABLE 10: Thermochemical Constants of the Gas-Phase Reactions and Dissociative and Substitutive Adsorption Reactions ($T = 573$ K)

no.	type of reaction	reaction
21	gas-phase	$SgCl_6(g) \leftrightarrow SgCl_5(g) + {}^1/_2Cl_2(g)$
22	dissociative adsorption	$SgCl_6(g) \leftrightarrow SgCl_5(ads) + {}^1/_2Cl_2(g)$
23	gas-phase	$SgCl_6(g) + {}^1/_2O_2(g) \leftrightarrow SgOCl_4(g) + Cl_2(g)$
24	substitutive adsorption	$SgCl_6(g) + {}^1/_2O_2(g) \leftrightarrow SgOCl_4 + Cl_2(g)$
25	gas-phase	$SgOCl_4(g) + {}^1/_2O_2(g) \leftrightarrow SgO_2Cl_2(g) + Cl_2(g)$
26	substitutive adsorption	$SgOCl_4(g) + {}^1/_2O_2(g) \leftrightarrow SgO_2Cl_2(ads) + Cl_2(g)$
27	gas-phase	$SgO_2Cl_2(g) + {}^1/_2O_2(g) \leftrightarrow SgO_3(g)$
28	substitutive adsorption	$SgO_2Cl_2(g) + O_2(g) \leftrightarrow SgO_3(ads) + Cl_2(g)$
29	gas-phase	$SgOCl_4(g) + {}^1/_2O_2(g) \leftrightarrow SgO_3 + 2Cl_2(g)$
30	substitutive adsorption	$SgOCl_4(g) + {}^1/_2O_2(g) \leftrightarrow SgO_3(ads) + 2Cl_2(g)$

reaction	Sg I ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	log *K*	Sg II ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	log *K*
21	+92.2	+104.5	+32.3	−2.95	+140.3	+104.5	+80.4	−7.33
22	+7.6	−64.3	+44.4	−4.05	+47.2	−64.3	+84.0	−7.66
23	−189.2	+79.4	−234.7	21.39	−213.4	+79.5	−263.4	24.05
24	−267.8	−89.1	−216.7	19.75	−304.6	−89.1	−253.3	23.09
25	−42.48	+105.5	−103.5	9.43	−39.8	+106.5	−100.8	9.19
26	−143.1	−61.5	−107.8	9.83	−152.9	−61.5	−117.7	10.73
27	+406.1	+52.5	+376.1	−34.28	+449.4	+52.5	419.3	−38.22
28	+10.2	−114.9	+76.0	−6.93	+5.6	−114.9	+71.4	−6.51
29	+363.6	+38.5	+341.6	+31.14	+409.6	+38.5	+387.6	+35.33
30	−32.3	−128.9	+41.6	−3.79	−34.2	−128.7	+39.7	−3.62

TABLE 11: Retention Times of Sg, Assuming Complex Adsorption Reactions at Different Concentrations of Oxygen and Chlorine[a]

Cl_2, $cm^3\ min^{-1}$ STP	retention time *t*, s			
	reaction 28		reaction 30	
	Sg I	Sg II	Sg I	Sg II
100	0.084	0.084	0.093	0.097
20	0.084	0.084	0.302	0.409
2	0.084	0.086	21.8	32.5
0.2	0.085	0.102	2.18×10^3	3.25×10^3
0.02	0.091	0.263	2.18×10^5	3.25×10^5
0.002	0.148	1.873	2.18×10^7	3.25×10^7
0.0002	0.782	17.972		

[a] Model parameters as in Table 9. O_2 flow is 3.66 $cm^3\ s^{-1}$, and the standard gas concentration is 2.6793×10^{19} cm^{-1}.

suitable chemical compounds for gas adsorption chromatographic experiments with Sg.

For a given chemical state of the species not only the composition of the gas phase is important. The adsorption behavior might also be influenced by dissociative or substitutive reactions, which might change the chemical state of the gaseous species during the process of adsorption.

No influence on the retention behavior of the molecules is expected if gas-phase reactions preferentially occur and if the products are not exhibiting considerably different adsorption properties. This is the case for reactions 21, 23, and 25 (Table 10). The trioxide is strongly adsorbed (see Table 8), while in the gas phase this state is remarkably unstable. Therefore, the gas-phase reactions 27 and 29 (Table 10) are thermodynamically not favored. The strong adsorption of SgO_3 strongly supports the possibility of a substitutive adsorption of $SgOCl_4$ and to a lesser extent of SgO_2Cl_2 by substituting chlorine with oxygen. In these cases the retention behavior depends on the composition of the gas phase. High concentrations of oxygen can lead to a preferential formation of the trioxide in the adsorbed state.

With eq 18 possible contributions of substitutive adsorption reactions to the retention behavior were estimated (Table 11). The factors f_c were deduced[41,42] assuming different compositions of the gas phase:

$$f_c\ (\text{reaction } 27) = \frac{c^{1/2}O_2(g)[c°(Cl_2(g))]^{1/2}}{c(Cl_2(g))} \tag{19}$$

and

$$f_c\ (\text{reaction } 29) = \frac{c(O_2(g))c°(Cl_2(g))}{c(Cl_2(g))} \tag{20}$$

The results show that only in reactive carrier gases with very high oxygen and low chlorine concentration is an influence on the retention behavior of Sg in quartz chromatography columns expected. At higher chlorine concentration formation of oxychlorides is favored. According to the data for reaction 25 (Table 10), the formation of SgO_2Cl_2 is dominating.

The knowledge of the entropy values allows an estimate of the temperature dependence of the reaction equilibria. The $SgCl_6$ dissociation reaction is strongly promoted by a temperature increase and can be shifted completely to the side of $SgCl_5$. A strong temperature dependence should occur in gas-phase reaction 25 so that with a Cl_2/O_2 ratio greater than 1 the state SgO_2Cl_2 is also more probable.

Because of the larger number of gaseous species on the right-hand side of the reaction equation, the entropies of complex adsorption reactions are, as a basic principle, smaller than the adsorption entropies of stable species (Tables 10). An increase of the temperature strongly shifts the reaction equilibrium toward an increased desorption of stable species, whereas for complex adsorption reactions this effect is less pronounced. With increasing temperature the gas-phase reaction equilibria of reactions 23, 27, and 29 are shifted to the right-hand side but are less pronounced than in reactions 21 and 25.

Because of their extrapolative character, the discussed values have to be regarded as rough estimates, which allow only a coarse evaluation of differences in the stability of compounds and of reaction probabilities. The problem, how to quickly bring a short-lived atom into a defined molecular state using a reactive carrier gas, how to stabilize that state, and how to characterize its gas chromatographic behavior, requires an experimental investigation. This was accomplished by studying the behavior of the smallest amounts of synthetic, short-lived nuclides of the homologue elements Mo and W in gas chromatographic separations.[7]

References and Notes

(1) Lazarev, Y. A.; Lobanov, Y. V.; Oganessian, Y. T.; Utyonkov, V. K.; Abdullin, F. S.; Buklanov, G. V.; Gikal, B. N.; Iliev, S.; Mezentsev, A. N.; Polyakov, A. N.; Sedykh, I. M.; Shirokovsky, I. V.; Subbotin, V. G.; Sukhov, A. M.; Tsyganov, Y. S.; Zhuchko, V. E.; Lougheed, R. W.; Moody, K. J.; Wild, J. F.; Hulet, E. K.; McQuaid, J. H. *Phys. Rev. Lett.* **1994**, *73*, 624−627.

(2) Schädel, M.; Brüchle, W.; Dressler, R.; Eichler, B.; Gäggeler, H. W.; Günther, R.; Gregorich, K. E.; Hoffman, D. C.; Hübener, S.; Jost, D. T.; Kratz, J. V.; Paulus, W.; Schumann, D.; Timokhin, S.; Trautmann, N.; Türler, A.; Wirth, G.; Yakushev, A. *Nature* **1997**, *388*, 55−57.

(3) Türler, A.; Dressler, R.; Eichler, B.; Gäggeler, H. W.; Jost, D. T.; Schädel, M.; Brüchle, W.; Gregorich, K. E.; Trautmann, N.; Taut, S. *Phys. Rev.* **1998**, *C57*, 1648−1655.

(4) Türler, A.; Buklanov, G. V.; Eichler, B.; Gäggeler, H. W.; Grantz, M.; Hübener, S.; Jost, D. T.; Lebedev, V. Ya.; Piguet, D.; Timokhin, S. N.; Yakushev, A. B.; Zvara, I. *J. Alloys Compd.* **1998**, *271−273*, 287−291.

(5) Türler, A.; Eichler, B.; Jost, D. T.; Piguet, D.; Gäggeler, H. W.; Gregorich, K. E.; Kadkhodayan, B.; Kreek, S. A.; Lee, D. M.; Mohar, M.; Sylwester, E.; Hoffman, D. C.; Hübener, S. *Radiochim. Acta* **1996**, *73*, 55−66.

(6) Gäggeler, H. W.; Jost, D. T.; Baltensperger, U.; Weber, A.; Kovacs, A.; Vermeulen, D.; Türler, A. *Nucl. Instrum. Methods Phys. Res.* **1991**, *A309*, 201−208.

(7) Gärtner, M.; Boettger, M.; Eichler, B.; Gäggeler, H. W.; Grantz, M.; Hübener, S.; Jost, D. T.; Piguet, D.; Dressler, R.; Türler, A.; Yakushev, A. B. *Radiochim. Acta* **1997**, *78*, 59−68.

(8) Gäggeler, H. W. *J. Alloys Compd.* **1998**, *271−273*, 277−282.

(9) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1995**, *99*, 144−147.

(10) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1994**, *98*, 6468−6473.

(11) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1996**, *100*, 8748−8751.

(12) Keller, O. L., Jr. *Radiochim. Acta* **1984**, *37*, 169−180.

(13) Eichler, B.; Domanov, V. P.; Zvara, I. *Evaluation of Heat of Adsorption Values from Thermochromatographic Data. II. Chlorides of Metals. The Adsorption on Quartz*; Report GSI-tr-4/76, JINR; Dubna: Darmstadt, 1976; Vol. P12, p 9454.

(14) Leibnitz, E.; Struppe, H. G. *Handbuch der Gaschromatographie*, 3rd ed.; Akademische Verlagsgesellschaft Geest & Portig K.-G.: Leipzig, 1984.

(15) Eichler, B.; Zvara, I. *Radochim. Acta* **1982**, *30*, 233−238.

(16) Zvara, I. *Radiochim. Acta* **1985**, *38*, 95−101.

(17) Mott, B. W. *J. Mater. Sci.* **1968**, *3*, 424.

(18) Ehrlich, G. *J. Chem. Phys.* **1959**, *31*, 111.

(19) Eley, D. D. *Ber. Bunsen-Ges. Phys. Chem.* **1955**, *60*, 797.

(20) Eichler, B. *Kernenergie* **1976**, *19*, 307.

(21) Eichler, B.; Gäggeler, H. W. Annual Report 1993; Paul Scherrer Institut, Labor für Radio- und Umweltchemie: Villigen, Switzerland, 1994; p 40.

(22) Eichler, B.; Rossbach, H. *Radiochim. Acta* **1983**, *33*, 121.

(23) Miedema, A. R. Z. *Metallkd. Aspekte Galvanotech., Ber. Symp.* **1978**, *69*, 287.

(24) Knacke, O.; Kubaschevski, O.; Hesselmann, K. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag und Verlag Stahleisen: Düsseldorf, 1991.

(25) Karapetjanz, M. Kh. *Osnovnie Termodinamiceskie Konstanty*; Izd. Khimija: Leningrad, 1968.

(26) Jackson, D. D. *Thermodynamics of the Gaseous Hydroxides*; UCRL-51 137, University of California, Lawrence Livermore, 1971.

(27) Gurvic, L. B. *Energija Razriva Khimiceskikh Svjazei*; Izd. Nauka: Moskva, 1974.

(28) Brewer, L.; Lammoreaux, R. H. *Thermochemical Properties*. In *Atomic Energy Reviews, Special Issue Nr. 7, Molybdenum, Physicochemical Properties of its Compounds and Alloys*; IAEA: Vienna, 1980; p 11.

(29) Oppermann, H.; Stöver, G.; Kunze, G. *Z. Anorg. Allg. Chem*. **1972**, *387*, 201.

(30) Wagman, D. D.; Evans, W. H.; Parker, V. P.; Schumm, R. H.; Halow, I.; Bailry, S. M.; Churney, K. L.; Nuttal, R. L. *J. Phys. Chem. Ref. Data, Suppl. 1* **1985**, 14.

(31) Schukarev, S. A.; Vasilkova, I. V.; Scharupin, R. N. *Vestn. Leningr. Univ*. **1961**, *4*, 130.

(32) Vahle, A.; Hübener, S.; Eichler, B. *Radiochim. Acta* **1995**, *69*, 233.

(33) Latimer, W. M. *J. Am. Chem. Soc*. **1951**, *73*, 1480.

(34) Schäfer, H.; Von Schnering, H. G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281.

(35) Chase, W.; Davis, C. A.; Downey, J. R., Jr.; Frurib, D. J.; McDonald, R. A.; Syverud, A. N. *Phys. Chem. Ref. Data, Suppl. 2* **1982**, 11.

(36) Eichler, B. Domanov, V. P. *J. Radioanal. Chem*. **1975**, *28*, 143.

(37) Penneman, R. A.; Mann, J. B. Proceedings of the Moscow Symposium on Chemical Transuranium Elements. *J. Inorg. Nucl. Chem., Suppl*. **1976**, 257.

(38) Oppermann, H. *Z. Anorg. Allg. Chem*. **1971**, *383*, 1.

(39) Efimov, A.I. *Svoistva neorganiceskikh soedinenie*; Izd. Khimija: Leningrad 1983.

(40) Gäggeler, H. W.; Dornhöfer, H.; Schmidt-Ott, W. D.; Greulich, N.; Eichler, B. *Radiochim. Acta* **1985**, *38*,103.

(41) Eichler, B. *Radiochim. Acta* **1996**, *72*, 19.

(42) Eichler, B.; Zude, F.; Fan, W.; Trautmann, N.; Herrmann, G. *Radiochim. Acta* 1**993**, *61*, 81.

(43) Evans, J. C.; Lo, G. J. S. *J. Mol. Spectrosc*. **1968**, *26*, 147.