

On the Stability and Volatility of Group 8 Tetroxides, MO₄ (M = Ruthenium, Osmium, and Hassium (Z = 108))

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Recently, an experiment to chemically characterize for the first time a compound of the transactinide element hassium (Hs, Z = 108) has been performed. On the basis of the assumption that Hs will belong to group 8 of the periodic table and will thus be homologous to ruthenium (Ru) and osmium (Os), the presumably very volatile HsO₄ was isolated by gas adsorption chromatography. The experiment allowed the determination of the enthalpy of adsorption ($-\Delta H_a^{0(T)}$) of HsO₄ on a silicon nitride surface. In this work, the trend in standard enthalpies of sublimation ($\Delta H_S^{0(298)}$) of group 8 element tetroxides established by ruthenium tetroxide and osmium tetroxide was extrapolated to hassium tetroxide. The $\Delta H_S^{0(298)}$ (HsO₄) was found to be very similar to $\Delta H_S^{0(298)}$ (OsO₄). On the basis of an empirical correlation between the sublimation enthalpies and the enthalpies of adsorption of oxide (and oxyhydroxide) molecules on quartz surfaces, $-\Delta H_a^{0(T)}$ (HsO₄) was predicted to be 46 ± 15 kJ mol⁻¹. A trend for the values of the adsorption enthalpies of RuO₄ \approx OsO₄ \approx HsO₄ was found. A different theoretical approach makes use of the relation between the interaction distance of a physisorbed, nonpolar molecule on a dielectric surface and the interaction energy. From literature values of the adsorption of noble gases on metal surfaces, it was found that this distance is independent of the adsorbed species, as well as of the adsorbent material. With the use of this universal interaction distance, $-\Delta H_a^{0(T)}$ (OsO₄) was calculated only from molecular geometries of OsO₄, the polarizability, and the first ionization potential and was found to agree with experimental results found in gas adsorption chromatography experiments. The $-\Delta H_a^{0(T)}$ values of RuO₄ and HsO₄ were calculated using the same procedure; where no experimental values of molecular properties were available, these were extrapolated or published values obtained from density functional calculations were used. A value of $-\Delta H_a^{0(T)}$ (HsO₄) = 47 ± 11 kJ mol⁻¹ is predicted, in agreement with the extrapolated value.

1. Introduction

The experimental chemical characterization of transactinide elements (Z \geq 104) is an extremely challenging task because these elements can only be produced at accelerators on a “one-atom-at-a-time” scale.¹ In addition, even the longest-lived known isotopes of these elements have half-lives of only a few minutes or seconds. Due to the minute production rates, experiments to investigate their chemical properties are very time-consuming. To date, the heaviest chemically characterized element is bohrium (Bh, Z = 107).² To proceed to the next heavier element hassium (Hs, Z = 108) it is necessary to carefully evaluate the expected chemical stability of Hs-containing molecules.

The first successful identification of three atoms of Hs after physical separation was reported in 1984 when the nuclide ²⁶⁵Hs (T_{1/2} = 1.55 ms) was produced in the heavy-ion-induced fusion reaction of ⁵⁸Fe and ²⁰⁸Pb at the Gesellschaft für Schwerionenforschung mbH in Darmstadt.³ A much more long-lived

isotope with mass number 269 was identified⁴ in the α decay chain of ²⁷⁷112 in 1996. A half-life of about 10 s was measured^{4,5} making this nuclide feasible for chemical investigations.

The elements in each group of the periodic table have a similar electronic structure and therefore exhibit similar chemical properties. Hassium is expected to be a member of group 8 of the periodic table and should thus behave homologously to Os and partly also like Ru. Well-known volatile compounds of Ru and Os are their tetroxides. Hence, also for Hs, the formation of a volatile tetroxide may be expected. Indeed, recently it was possible to show that in an oxygen-containing gas, a very volatile molecule of Hs, most likely HsO₄, could be produced.⁶ The experiment yielded an adsorption enthalpy of $-\Delta H_a^{0(T)}$ (HsO₄) = 46 ± 2 kJ mol⁻¹ on silicon nitride surfaces on the basis of only seven detected atoms. It was concluded that the interaction of HsO₄ with a dielectric surface is significantly stronger than the one of OsO₄.⁶ The influence of the surface material appeared to be negligible for physisorption processes on dielectric surfaces such as silicon oxides or nitrides as was concluded from comparable adsorption enthalpies of OsO₄ on these two surfaces.⁶ To interpret thermochemical data of transactinides, it is instrumental to make predictions based on the knowledge of homologous compounds. One approach is to perform

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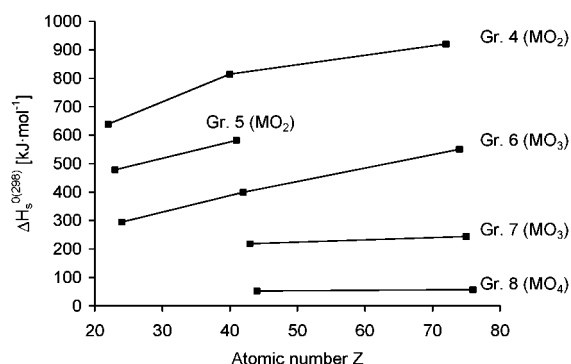


Figure 1. Standard sublimation enthalpies calculated from standard formation enthalpies as a function of the atomic number of mononuclear d element oxides of groups 4–8 in which the metal is in the highest possible oxidation state. Data are taken from refs 30–36.

relativistic density functional calculations of molecular properties as was recently reported for group 8 tetroxides.⁷ Application of semiempirical models for the interaction of HsO_4 with a quartz surface⁷ predicted a sequence $\text{RuO}_4 > \text{OsO}_4 \geq \text{HsO}_4$ for $-\Delta H_a^{0(T)}$.

In this work, predictions on the stability and volatility, that is, the sublimation enthalpy, of oxide compounds of group 8 elements are made on the basis of thermodynamical extrapolations. In a second part, the adsorption behavior of tetroxide molecules of group 8 elements on a quartz surface is predicted assuming physisorption on a dielectric surface. Finally, the predicted adsorption enthalpies are compared with experimental data.

2. Extrapolation of Chemical Properties from RuO_4 and OsO_4 to HsO_4

Within the groups, there exist trends in chemical properties that usually are followed when going from one period to the next one. As an example, the standard enthalpies of sublimation ($\Delta H_s^{0(298)}$) of mononuclear oxides of d elements with the highest possible oxidation states of the metals exhibit trends for the elements of groups 4–8 (see Figure 1). The data depicted in Figure 1 are differences of the standard formation enthalpies of the solid and the gaseous species. The reason for the observed increasing sublimation enthalpies with atomic number is that the stability of the solid state increases more strongly than the stability of the gaseous state. However, this trend holds only for group 4, 5, and 6 oxides. For group 7 and 8 oxides, $\Delta H_s^{0(298)}$ seems to be independent of the atomic number. On the basis of this simple picture, it is expected that $\Delta H_s^{0(298)}$ of HsO_4 should be very similar to that of OsO_4 and RuO_4 .

The standard enthalpy of sublimation, $\Delta H_s^{0(298)}$, is a measure for the volatility of a compound. Gas-phase experiments with carrier-free amounts have clearly proven that excellent linear empirical correlations exist between $\Delta H_s^{0(298)}$ values for a given class of compounds (e.g., oxides) and measured retention temperatures.⁸ From the latter, adsorption enthalpies ($-\Delta H_a^{0(T)}$) may be calculated, and hence, $\Delta H_s^{0(298)}$ and $-\Delta H_a^{0(T)}$ can be directly linked.⁹

2.1. Stability and Volatility of Oxides. Standard formation enthalpies and standard entropies of O, O_2 , Ru, and Os and their oxides and some other physicochemical data used in this work are summarized in Tables 1 and 2.

Empirical linear correlations were found between different thermochemical properties and molecular characteristics (e.g., molar volumes or radii) of compounds in several groups of the

TABLE 1: Standard Formation Enthalpies and Standard Entropies of Oxygen, Ruthenium, Osmium, Ruthenium Oxides, and Osmium Oxides Used in This Work

compound	ΔH_f^0 [kJ mol ⁻¹]	ref	ΔS_f^0 [J mol ⁻¹ K ⁻¹]	ref
O(g)	249.2 ± 0.1	37	160.95 ± 0.02	37
O ₂ (g)	0		205.0	37
Ru(s)	0		26.86	37
Ru(g)	+648.5 ± 5.4	38	186.5	38
RuO(s)				
RuO(g)	+372 ± 42	31	242	31
RuO ₂ (s)	-313.52 ± 0.08	39	46.15 ± 0.05	40
RuO ₂ (g)	+119 ± 10	31,41	265 ± 5	31
RuO ₃ (s)	-251	38	79.5 ± 6	38
RuO ₃ (g)	-70.8 ± 6.6	31	285.8 ± 8.4	31
RuO ₄ (s)	-244.4 ± 4.4	31	154.0 ± 1.1	31
RuO ₄ (g)	-192.7 ± 4.0	31	290.6 ± 0.6	31
Os(s)	0		32.7	35,40
Os(g)	784.6 ± 3.8	38	191.8 ± 2.5	38
OsO(s)				
OsO(g)	> +448	42		
OsO ₂ (s)	-295.96 ± 0.08	39	49.8 ± 0.2	39
OsO ₂ (g)	+193	42		
OsO ₃ (s)	-190.5	42		
OsO ₃ (g)	-167.5 ± 12.6	35	276	35
OsO ₄ (s)	-394 ± 8	35	137 ± 8	35
OsO ₄ (g)	-337 ± 8	35	293.9 ± 0.3	35

periodic table, for example, groups 6 (including seaborgium (Sg, Z = 106))¹⁰ and 7 (including Bh).¹¹

As a reference for the extrapolation of formation enthalpies, the standard enthalpies of the gaseous monatomic elements $\Delta H^{0(298)}(\text{M})_{(g)}$ were used. Because an accurate prediction of $\Delta H^{0(298)}(\text{Hs})_{(g)}$ is difficult, a realistic range limited by two values for $\Delta H^{0(298)}(\text{Hs})_{(g)}$, denoted by Hs I and Hs II, was chosen. The value $\Delta H^{0(298)}(\text{Hs I})_{(g)} = 790$ kJ mol⁻¹ was predicted by Eichler¹² on the basis of a linear extrapolation. Another calculation performed by Fricke¹³ yielded $\Delta H^{0(298)}(\text{Hs II})_{(g)} = 842$ kJ mol⁻¹. A value nearly identical to $\Delta H^{0(298)}(\text{Hs I})_{(g)}$ of 791 kJ mol⁻¹ has been calculated by Ionova et al.¹⁴ on the basis of a semiempirical model, which is primarily based on the estimation of trends in $\Delta H_s^{0(298)}$ in the transactinide series. The trends were shown to be governed by the ground-state electronic configuration of the atom in the free and the metallic state. (In ref 15, a value of 628 kJ mol⁻¹ is erroneously cited from ref 16 as $\Delta H^{0(298)}(\text{Hs})_{(g)}$ instead of correctly $\Delta G^{0(298)}(\text{Hs})_{(g)}$.)

In the next step, the atomic formation enthalpies of the gaseous and solid oxides $\Delta H^*(\text{MO}_x)_{(g,s)}$ were determined with

$$\Delta H^*(\text{MO}_x)_{(g)} = \Delta H^{0(298)}(\text{MO}_x)_{(g)} - \Delta H^{0(298)}(\text{M})_{(g)} - x\Delta H^{0(298)}(\text{O})_{(g)} \quad (1)$$

$$\Delta H^*(\text{MO}_x)_{(s)} = \Delta H^{0(298)}(\text{MO}_x)_{(s)} - \Delta H^{0(298)}(\text{M})_{(g)} - x\Delta H^{0(298)}(\text{O})_{(g)} \quad (2)$$

and are shown in Figure 2 as a function of the standard enthalpy of the gaseous metals ($\Delta H^{0(298)}(\text{M})_{(g)}$). Also included are linear extrapolations for Hs I and Hs II. The slopes and intercepts of the extrapolations are listed in Table 3.

Because the $\Delta H^{0(298)}(\text{M})_{(g)}$ values are already included in the quantities of $\Delta H^*(\text{MO}_x)_{(g,s)}$, the stability of the compound MO_x increases with increasing atomic number if the slope of the correlation of $\Delta H^*(\text{MO}_x)_{(g,s)}$ against $\Delta H^{0(298)}(\text{M})_{(g)}$ for elements of a given group is larger than one. It therefore follows for the gaseous and solid tetroxides that the stability increases from RuO_4 to OsO_4 . Consequently, HsO_4 is expected to be thermodynamically even more stable, as has also been predicted in ref 7.

TABLE 2: Compilation of Relevant Physicochemical Data Used in This Work

parameter	RuO ₄	ref	OsO ₄	ref	HsO ₄	ref
polarizability, α [cm ³]	$(7.92 \pm 0.15) \times 10^{-24}$	<i>a</i>	8.17×10^{-24}	43	8.46×10^{-24}	7 ^b
first ionization potential, IP ₁ [eV]	12.33 ± 0.23	44	12.97 ± 0.12	44	12.27	7
molar weight, M [g mol ⁻¹]	165.1	30	254.2	30		
density, ρ [g cm ⁻³]	3.29	30	5.1	30		
critical volume, V_c [cm ³ mol]			156.93	45		
critical density, ρ_c [g cm ⁻³]			1.62	45		
subl enthalpy, $\Delta H_S^{0(298)}$ [kJ mol ⁻¹]	51.7 ± 5.9	31 ^c	57 ± 11	35 ^c		
			59.95 ± 0.25	35 ^d		
symmetry group	T_d	37	T_d	37		
distance M–O [nm]	0.171 ± 0.0003	37	0.171 ± 0.0003	37		
angle O–M–O [deg]	109.5	37	109.5	37		
<hr/>						
			SiO ₂		ref	
dielectric constant, ϵ			3.81		46	
first ionization potential, IP ₁ [eV]			11.7 ± 0.5		42	

^a This work. ^b Adjusted value, see text. ^c Calculated from formation enthalpies cited therein. ^d Experimental value.

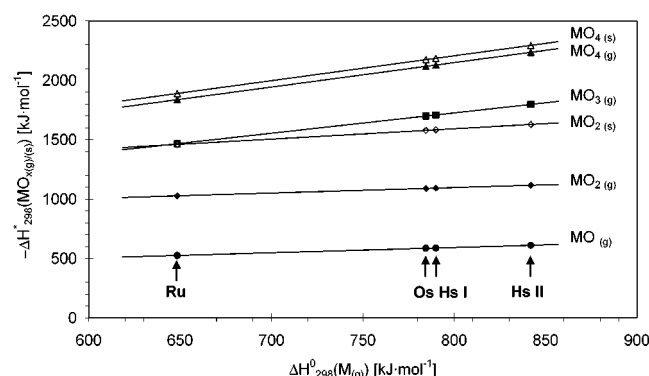


Figure 2. Atomic formation enthalpies of the gaseous and solid oxides of group 8 elements as a function of the standard enthalpy of the gaseous metals (slopes and intercepts are summarized in Table 3). MO_{3(s)} and MO_{3(g)} are unknown.

TABLE 3: Constants of the Linear Regression Analysis between Atomic Formation Enthalpies of Oxides (s,g) and the Atomic Formation Enthalpy of the Gaseous Metal

	MO _{1(g)}	MO _{2(g)}	MO _{3(g)}	MO _{4(g)}	MO _{2(s)}	MO _{4(s)}
slope	0.44	0.46	1.71	2.06	0.87	2.10
intercept [kJ mol ⁻¹]	239.30	731.05	357.64	501.93	895.59	530.28

The $\Delta H_S^{0(298)}$ value can be deduced from the atomic formation enthalpies as

$$\Delta H_S^{0(298)}(\text{MO}_x) = \Delta H^*(\text{MO}_x)_{(g)} - \Delta H^*(\text{MO}_x)_{(s)} \quad (3)$$

which yields $\Delta H_S^{0(298)}(\text{HsO}_4) = 57 \pm 11$ and 58 ± 13 kJ mol⁻¹ for Hs I and Hs II. These values agree within the error limits with the $\Delta H_S^{0(298)}$ values for OsO₄ of 57 and 60 kJ mol⁻¹ (see Table 2).

2.2. Relation between Sublimation Enthalpy and Adsorption Enthalpy. A good empirical linear correlation was found between the standard sublimation enthalpy ($\Delta H_S^{0(298)}$) of macroscopic amounts of a number of oxides and oxyhydroxides and their respective adsorption enthalpy on quartz surfaces ($-\Delta H_a^{0(T)}$), measured for carrier-free amounts.⁸ An updated correlation that takes into account also more recent experiments resulted in⁹

$$-\Delta H_a^{0(T)} = (6.3 \pm 7.8) + (0.680 \pm 0.028) \cdot \Delta H_S^{0(298)} \quad (4)$$

Applying eq 4 to the values for $\Delta H_S^{0(298)}$ listed in Table 2 for

TABLE 4: Enthalpies and Entropies of Adsorption of RuO₄ and OsO₄ Evaluated in Gas Adsorption Chromatography Experiments with Carrier-Free Amounts Described in Literature^a

compound	$-\Delta H_a^{0(T)}$ [kJ mol ⁻¹]	$\Delta S_a^{0(T)}$ [J mol ⁻¹ K ⁻¹]	experimental method	ref
RuO ₄	55.0 ± 4.2	-168.7 ± 0.5^b	off-line	47
			thermochromatography	
	10.7 ± 1.7	-139.9 ± 3.1	isothermal gas chromatography	29
OsO ₄	39 ± 1	-170.5^b	on-line thermochromatography	6
	50 ± 5	-180^c	off-line thermochromatography	8
	41 ± 2	-180^c	on-line thermochromatography	26
	57 ± 4	-180^c	off-line thermochromatography	26
	9.8 ± 2.0	-157.5 ± 6.8	isothermal gas chromatography	29
	38.0 ± 1.5	-170.5^b	isothermal gas chromatography	27
	40.2 ± 1.5		on-line thermochromatography	28

^a The surface material was SiO₂ in refs 8, 26–29, and 47 and Si₃N₄ in ref 6. The standard states were the same in all references except in ref 29. ^b Calculated according to the model of mobile adsorption (ref 20). ^c Assumed as -180 J mol⁻¹ K⁻¹ for the evaluation of $-\Delta H_a^{0(T)}$.

OsO₄ and RuO₄ yields $-\Delta H_a^{0(T)}$ values of 45 ± 15 and 41 ± 12 kJ mol⁻¹. These values agree reasonably well with literature values from gas adsorption chromatography experiments (Table 4).

By using the average value for Hs I and Hs II for $\Delta H_S^{0(298)}(\text{HsO}_4)$ and applying eq 4, $-\Delta H_a^{0(T)}(\text{HsO}_4) = 46 \pm 15$ kJ mol⁻¹ is derived. The following trend for the volatility of the group 8 tetroxides is therefore expected: RuO₄ \approx OsO₄ \approx HsO₄.

3. A Model for the Physisorption of Volatile Molecules on Dielectric Surfaces

In the following, an independent approach is made to describe the adsorption of a group 8 tetroxide molecule with a physisorption model and an assumed equivalence of the sorption process to that of noble gases.

3.1. Adsorption of Polarizable Molecules. The interaction energy of molecules without a permanent dipole moment with a dielectric solid involves mainly dispersion forces. Attraction

due to physisorption forces can be written in the form¹⁷

$$E_B = -\frac{C_1}{r^6} \quad (5)$$

where E_B is the interaction energy in electronvolts, C_1 is the van der Waals constant between two systems 1 and 2, and r is the interaction distance in centimeters.

The total interaction energy between a molecule and a two-dimensional surface of infinite extent can be obtained by a summation over all molecule–molecule interactions.¹⁷ This summation can be replaced by a triple integration.¹⁷ Equation 5 then has the form¹⁷

$$E_B = -\left(\frac{\pi}{6}\right)NC_1\frac{1}{r^3} \quad (6)$$

where N is the number of atoms per cubic centimeter.

Generally for two different types of interacting molecules, 1 and 2, C_1 is¹⁸

$$C_1 = \frac{3}{2}\alpha_1\alpha_2\frac{E_{DT(1)}E_{DT(2)}}{E_{DT(1)} + E_{DT(2)}} \quad (7)$$

where the α parameters are the polarizabilities of the molecules 1 and 2 in cubic centimeters and E_{DT} is the average dipole transition energy of the molecules in electronvolts. The polarizability of quartz can be calculated from the well-known equation for solids⁷

$$\alpha_2 = \frac{3}{4\pi N} \frac{(\epsilon - 1)}{(\epsilon + 2)} \quad (8)$$

where ϵ is the dielectric constant of the solid. Introducing eqs 7 and 8 into eq 6 yields

$$E_B = \frac{3\alpha}{16r^3} \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{E_{DT(1)}E_{DT(2)}}{E_{DT(1)} + E_{DT(2)}} \quad (9)$$

Pauling empirically found the average dipole transition energy, E_{DT} , to be a function of the first ionization potential, IP_1 :¹⁹

$$E_{DT} = 1.57IP_1 \quad (10)$$

where IP_1 is the first ionization potential in electronvolts.

The value of E_B cannot be measured directly, but in gas adsorption chromatographic measurements, $-\Delta H_a^{0(T)}$ of the species on the surface material is usually evaluated (Table 4). The relation between $\Delta H_a^{0(T)}$ and E_B can be understood as follows (Figure 3): To remove a molecule with zero degree of freedom (no translatory or vibrational degrees of freedom, i.e., “frozen-state approximation”) from the surface to an infinite distance, the energy E_B is needed. If the molecule then is released from its frozen state into the gaseous phase, three translatory degrees of freedom have to be added, requiring an energy of $1.5RT$. In the model of mobile adsorption²⁰ (right-hand side of Figure 3), an energy of $\Delta H_a^{0(T)}$ is gained when a molecule from the gaseous phase is adsorbed to the surface. This adsorbed state differs from the frozen-state approximation by having one vibrational and two translatory degrees of freedom. The energy of the vibrational degree of freedom amounts to RT , and the energy of each translatory degree of freedom amounts to $0.5RT$. Therefore,

$$E_B = -\Delta H_a^{0(T)} + 0.5RT \quad (11)$$

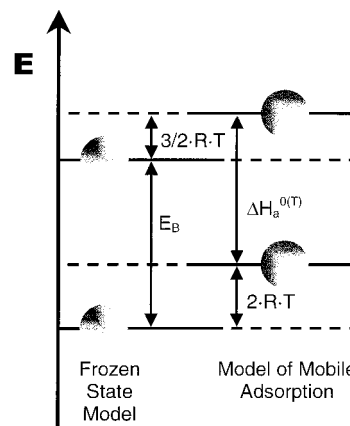


Figure 3. Relation between E_B and $\Delta H_a^{0(T)}$. For explanations, see text.

TABLE 5: Adsorption Distances of Noble-Gas Atoms on Metal Surfaces Using Data from Refs 21 and 22

noble gas	mean r [nm]	std dev [nm]	number of values
Ne	0.2342	0.0036	3
Ar	0.2533	0.0198	5
Kr	0.2636	0.0197	14
Xe	0.2393	0.0188	29
Rn	0.2452		1
mean	0.247	0.020	52

3.2. Calculation of the Adsorption Distances of Noble Gases. The distances of noble gases adsorbed on metal surfaces were calculated¹⁸ using experimental adsorption data^{21,22} of the noble gases Ne, Ar, Kr, Xe, and Rn on 15 different metal surfaces. The results are summarized in Table 5 and show that r is independent of the noble gas and the adsorbent metal. Thus, the assumption of a mean value of $r = 0.247 \pm 0.020$ nm seems to be justified, and we therefore assume this universal adsorption distance for symmetrical molecules and noble-gas atoms.

3.3. Application of the Model to OsO₄. Because of the coordinative saturation of the metal ions in symmetrical molecular geometries such as the tetrahedral group 8 tetroxides, the interaction of these compounds with surfaces is dominated by physisorptive forces. We therefore assume that this process can be treated similarly to the sorption process of noble gases to surfaces. The universal distance r given above is slightly larger than the “size” of the OsO₄ molecule characterized by the van der Waals radius, r_{vdW} (ref 23),

$$r_{vdW} = \left(\frac{3b}{16\pi N_0}\right)^{1/3} \quad (12)$$

with r_{vdW} = the van der Waals radius [cm], b = the van der Waals constant [cm³], and N_0 = Avogadro’s number (6.022×10^{23}). The value of the van der Waals constant, b , can be derived from²³

$$b = \frac{V_c}{3} \quad (13)$$

with V_c = the critical molar volume [cm³ mol^{−1}].

For OsO₄ with a van der Waals constant b of 52.31 cm³ mol^{−1}, $r_{vdW}(\text{OsO}_4) = 0.1731$ nm is obtained. Comparison with data of the noble gases^{24,25} shows that $r_{vdW}(\text{Xe}) < r_{vdW}(\text{OsO}_4) < r_{vdW}(\text{Rn})$.

Using $r = 0.247 \pm 0.020$ nm, $E_B(\text{OsO}_4)$ can be evaluated with eq 9 using data from Table 2 as $E_B(\text{OsO}_4)_{\text{calcd}} = 0.47 \pm$

TABLE 6: Summary of Theoretical and Experimental Values for $-\Delta H_a^{0(T)}$ of OsO₄ and HsO₄

method	$-\Delta H_a^{0(T)}(\text{OsO}_4)$ [kJ mol ⁻¹]	$-\Delta H_a^{0(T)}(\text{HsO}_4)$ [kJ mol ⁻¹]	ref
linear extrapolation	45 ± 15	46 ± 15	this work
physisorption model	47 ± 11	47 ± 11	this work
relativistic DFT + interaction model	38.0 ± 1.5 ^a	35.9 ± 1.5	7
experiment	39.6 ± 1.3 ^b	46 ± 2	6

^a Value (experimental result from ref 27) used as reference point.^b Average value of on-line experiments (refs 6, 26–28).

0.11 eV. Subsequently, $-\Delta H_a^{0(T)}(\text{OsO}_4)_{\text{calcd}} = 47 \pm 11$ kJ mol⁻¹ is calculated using eq 11. This value agrees within the error limits with experimental values^{6,26–28} obtained in on-line gas-chromatography experiments on silicon oxide and silicon nitride summarized in Table 4, which yielded an average value of $-\Delta H_a^{0(T)}(\text{OsO}_4)_{\text{expt}} = 39.6 \pm 1.3$ kJ mol⁻¹ and also with the value 45 ± 15 kJ mol⁻¹ deduced in section 2.2.

3.4. Extrapolation of the Adsorption Enthalpies for RuO₄ and HsO₄. There exists no experimental information on the polarizability of RuO₄. Comparison of the bond lengths, the molar volumes, and the volatilities shows that RuO₄ closely resembles OsO₄. The polarizability of RuO₄ can therefore be estimated under the assumption that it is proportional to the molar volume, the bond length, and the sublimation enthalpy normalized to those of OsO₄. Averaging the three values followed by multiplication with the polarizability of OsO₄ yields $\alpha(\text{RuO}_4) = (7.92 \pm 0.15) \times 10^{-24}$ cm³. In ref 7, $\alpha(\text{RuO}_4)$ has been calculated by different methods as 6.48×10^{-24} and 6.77×10^{-24} cm³.

With $\alpha = (7.92 \pm 0.15) \times 10^{-24}$ cm³, $-\Delta H_a^{0(T)}(\text{RuO}_4) = 44 \pm 11$ kJ mol⁻¹ is obtained with eqs 9 and 11 using the values given in Table 2 and assuming a “universal” r of 0.247 ± 0.020 nm, and subsequently, $\Delta H_S^{0(298)}(\text{RuO}_4) = 55 \pm 28$ kJ mol⁻¹.

Pershina et al.⁷ calculated $\text{IP}_1(\text{HsO}_4) = 12.27$ eV and $\alpha(\text{HsO}_4) = 6.26 \times 10^{-24}$ cm³. Because the agreement of $\alpha(\text{OsO}_4)$ calculated by the same procedure with experimental data was rather poor, the obtained values have been adjusted by the authors by using the experimental value of $\alpha(\text{OsO}_4)$ as a reference. A value of $\alpha(\text{HsO}_4) = 8.46 \times 10^{-24}$ cm³ is therefore recommended in ref 7. With the use of this value and $r(\text{HsO}_4) = 0.247 \pm 0.020$ nm, $-\Delta H_a^{0(T)}(\text{HsO}_4) = 47 \pm 11$ kJ mol⁻¹ is calculated. From this value, $\Delta H_S^{0(298)}(\text{HsO}_4) = 60 \pm 28$ kJ mol⁻¹ follows with eq 4. These values agree within the error limits with the ones obtained by the linear extrapolation method in section 2.2.

4. Conclusions

Two independent methods were applied to predict the adsorption behavior of HsO₄ on quartz surfaces. The first bases on a thermodynamic extrapolation of sublimation enthalpies of group 8 tetroxides from which adsorption enthalpies are deduced on the basis of an empirical correlation. The second approach describes the sorption process with a physisorption model of polarizable molecules, assuming a “universal” adsorption distance. Table 6 summarizes the adsorption enthalpies for OsO₄ and HsO₄ from this work in comparison with literature values based on a fully relativistic calculation, as well as with a recent experiment.

As can be seen, the values derived in this work agree with each other within the error limits, as well as with those found in ref 7 and experimental results. However, there seems to be

a systematic difference of the experimental values depending on the technique used. While all experimental $-\Delta H_a^{0(T)}(\text{OsO}_4)$ values obtained in the on-line regime lie around 40 kJ mol⁻¹ (refs 6, 26–28), the ones obtained in off-line experiments^{8,26} are higher by about 10–15 kJ mol⁻¹ (except the ones of ref 29 in which a different standard state was used). Probably, the sticking coefficient (probability of a species hitting the surface to adsorb) is smaller than one. This influence is more pronounced in experiments with high gas-flow rates (on-line experiments). It is therefore important to compare only $-\Delta H_a^{0(T)}$ values obtained under similar experimental conditions.

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