K_d -Value Determination for ²⁶¹Rf (Element 104) with the Multi-Column Technique

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After online experiments with ¹⁶⁵Hf ($t_{1/2} = 76$ s, decaying into ¹⁶⁵Lu) at GSI [1] we performed two experiments with the multi-column-technique [2] with Rutherfordium.

 261 Rf was produced in the 248 Cm(18 O, 5n) reaction at the PSI Philips Cyclotron. A 730 µg/cm² ²⁴⁸Cm target was bombarded with a 0.5 μA_{part} ¹⁸O⁵⁺ beam. The KCl aerosols transporting the activities was continuously dissolved in a degasser with a yield > 80% at a tolerable pressure in the target chamber of 1.7 bar at a gas-flow rate of 1.6 - 1.7 L/min and a distance between the target chamber and the degasser of approximately 50 m. The hold-up time of the activity in the degasser was about 2 s. A solution-level of 50 to 150 µL was kept at the bottom of the degasser through control by a light barrier which caused, if activated, an adjustment of the flow rate from the HPLC pump that pumped the solution into the degasser. The active solution leaving the degasser was pumped by a double-piston HPLC pump at a flow rate of 1 mL/min through a capillary of 0.3 mm inner diameter to three columns connected sequentially: A cation filter followed by the true chromatographic column filled with an anion-exchange resin, the latter followed by another cation filter.

Two experiments were performed, one using 0.5 M HF/0.1 M HNO₃ as the mobile phase, another one using 0.01 M HF (without any HNO₃). The running time was 24 hours in both cases. In the first case, the cation-exchange columns were filled with 330 mg of DOWEX 50WX8, minus 400 mesh. These filters were used for 3 hours and were then replaced by new ones. This ensured that there was no break-through by any of the descendants of 261 Rf, i.e. 257 No, 253 Fm, and 253 Es. The anion-exchange column was filled with 50 mg of DOWEX 1X8, minus 400 mesh in the nitrate form.

17 mg of DOWEX 1X8 in the fluoride form was used in the experiment with 0.01 M HF. In this experiment, 68 mg of DOWEX50WX8 were used as cation filters for running times of 4 hours. The effluent from the final cation filter was collected in a reservoir (activity AE).

After the end of the experiment, the final cation filter was stripped with 5 M HNO₃ (activity AD). The solutions AE and AD were spiked with ²⁴¹Am. After adjusting its pH to 2, the solution containing AE was passed over a cation-exchange column where ²⁵³Fm and ²⁵³Es were sorbed. This column and the cation-exchange columns containing AD were stripped with 5 M HNO₃ and the solutions were evaporated to dryness. The residues were dissolved in 8 M HCl and iron (from the steel capillary of the gas jet) was extracted into Aliquat 336 in chloroform. After evaporation to dryness of the aqueous phases, the residues were dissolved in 10 µl of 0.1 M HNO₃ and transferred into isopropanol for molecular plating. The latter was performed with 1200 V onto thin Ti foils of 430 µg/cm² thickness. These were subject to α spectroscopy in 4- π -geometry for more than 60 days, three half-lives of ²⁵³Es.

Overall chemical yields determined via the ²⁴¹Am activity (E_{α} =5.5 MeV) were 65% on the average. The background in the relevant energy window near 6.6 MeV was 1.5 α events per week.



Fig 1: α -energy spectrum of sample AD in experiment 2 with the 253 Es energy window indicated by arrows.

In the first experiment using 0.5 M HF/ 0.1 M HNO₃, the entire ²⁵³Es activity (80 events) was found in AE and no activity above background in AD indicating that the retention time of rutherfordium on the anion-exchange column must have been very short. From the activities, a $\underline{K_d} = 0^{+3}$ _0 mL/g results in 0,5 M HF / 0,1 M HNO₃. This is lower than the K_d value of ~5 determined with ARCA [3]. This is no major problem as it is known that K_d values < 10 are difficult to determine with ARCA and tend to be systematically high.

In the second experiment using 0.01 M HF (without HNO₃), we observed 90 events attributable to ²⁵³Es in AD while no events above background were detected in AE. This leads within 1 standard deviation to a K_d value of **394**^{+∞}₋₁₀₀ **mL/g** in good agreement with data taken offline by ARCA [4]. The error limits on the K_d values were determined by a Monte-Carlo simulation assuming a half life of ²⁶¹Rf of 78⁺¹¹₋₆ s [5] and a background due to electronic noise of 1.5 events per week in the interesting energy region (E_q=6.6 MeV).

These on-line experiments with 261 Rf corroborate the interesting finding [3,4] that the sensitivity of Rf fluoride complexes to the presence of the counter ion NO₃⁻⁻ is much more pronounced than for the fluoride complexes of the lighter homologs Zr and Hf.

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Fluoride Complexation of Rutherfordium (Rf, Element 104)

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The distribution coefficient (K_d) of ²⁶¹Rf on ion exchange resins at various HNO₃/HF concentrations had been studied [1]. Rf was eluted at higher HF concentrations from CIX than Zr and Hf and rather resembled Th. Up to 1 M HF, Rf was not retained on the AIX also resembling its pseudo-homolog Th.

Th is known to form no anionic fluoride complexes, while Zr and Hf are forming complexes of the type $[MF_6]^{2-}$ in HF solutions and therefore can be resorbed on AIX resins.

We have continued these studiesNow of Rf and on-line produced Hf by systemetically varying both the HNO₃ and the HF concentration. If Rf is resembling Th, there should exist no concentration range in which Rf is adsorbed on the AIX.

²⁶¹Rf was produced in the ²⁴⁸Cm(¹⁸O,5n) reaction at the PSI Philips Cyclotron. A 730 µg/cm² ²⁴⁸Cm target was bombarded with a 0.5 μA_{part} ¹⁸O⁵⁺ beam. The target contained 10% Gd thus producing simultaneously short-lived Hf isotopes. Rf and Hf were transported by a He(KCl) gas jet and collected for 90 s by impaction on a slider in the Automatic Rapid Chemistry Apparatus ARCA II. The residue was dissolved in 200 µl 0.1 M HNO₃/x M HF (x variable) and fed onto the AIX. The effluent was evaporated to dryness as sample 1. In order to elute remaining Rf from the column, a second fraction (200 µl) was collected which is known to elute group 4 elements from the column (2 M HCl/0.01 M HF). This fraction was prepared as sample 2. 78-s 261 Rf was detected by α -spectroscopy. The counting time was 12 min. Every 8th pair of samples was monitored by additional γ -spectroscopy to determine the distribution of Hf. From the ratio of the counting rates, the K_d values were calculated.

The results are shown in in the table and are also plotted in the 3D graphs below (some values in the plot are interpolated).

It is obvious that the behavior of Rf and Hf in the examined system are remarkably different. While the K_d values of Rf are varying strongly with both HF and HNO₃ concentration, the dependence of the Hf K_d values on the acid concentrations is rather weak.

[HNO ₃]	[HF]	$\log K_d(Hf)$	$\log K_{d}(Rf)$
0.1	0.01	2.1	0.8
0.1	0.03	2.1	0.9
0.1	0.05	2.0	0.8
0.1	0.5	2.1	0.9
0.1	1	2.2	0.7
0.03	0.5	2.2	1.7
0.01	0.01	2.1	1.0
0.01	0.05	2.3	1.6
0.01	0.5	2.5	1.6
0.003	0.5	2.7	1.7
0	0.01	2.5	2.7
0	0.1	2.7	2.4
0	0.5	2.8	1.8

Table: log K_d values of Hf and Rf in different media

Strong adsorption of both elements onto AIX can only be observed in pure HF solutions with concentrations [HF] > 0.01 M. This indicates the presence of anionic complexes under this condition which is in agreement with [3].

On the other hand, the sorption of the complexes on AIX seems to be influenced by the presence of other anions acting as counter ions on the exchanger resin (NO₃⁻ and/or HF₂⁻, see [2]).

Thus, Rf shows the typical behavior of group 4 (formation of anionic fluoride complexes), but the interaction of these complexes with different counter ions is enhanced with respect to Zr and Hf.

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Fig.1: Sorption of Hf in HNO₃/HF solutions on a AIX resin (Aminex A27 or Riedel de Haën).

Fig.2: Sorption of Rf in HNO₃/HF solutions on a AIX resin (Aminex A27 or Riedel de Haën).

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Theoretical Treatment of Fluoride Complexation of Element 104 in HF Solutions

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Recent experiments on fluoride complexation of element 104, Rf, in aqueous HF/HNO₃ solutions [1,2] have demonstrated an unexpected behaviour of Rf in comparison with that of Zr and Hf: Whereas all the elements are retained as cations on cation exchange resins (CIX) below 10^{-3} HF, no rise of the K_d value of Rf is observed up to 1M HF in contrast to Zr and Hf when sorbed by anion exchange resins (AIX). This observation was tentatively interpreted as a difference in the competition between NO₃⁻ with respect to RfF_x^{(x-4)-} on the one hand, and to ZrF_x^{(x-4)-} and HfF_x^{(x-4)-} on the other hand, for the binding sites on the AIX.

To interpret the unexpected behaviour of Rf in HF/HNO_3 solutions, we have studied the complex formation of Zr, Hf, and Rf theoretically using the model applied by us for prediction of complexation of element 105, Db, and element 106, Sg, in aqueous solutions [3,4].

In HF/HNO₃ solutions at HF between 10^{-3} M and 10^{-2} M HF/0.1 M HNO₃, at pH \cong 1, the complex formation can be described by the following equilibria

$$M(H_2O)_8^{4+} \Leftrightarrow MF(H_2O)_7^{3+} .. \Leftrightarrow .. MF_5(H_2O)^{-} \Leftrightarrow MF_6^{2-}$$
 (1)

where M = Zr, Hf, and Rf. To predict the complex formation, the free energy change ΔG^r of equilibria (1) should be calculated. As an initial step, the following equilibrium was considered

$$M(H_2O)_8^{4+} + 6HF \Leftrightarrow MF_6^{2-}$$
 (2)

According to our model, ΔG^r of a reaction can be expressed as

$$-\Delta G^{r}/2.3RT = \Delta \sum a_{i} + \Delta \sum a_{ij} - \Delta S, \qquad (3)$$

where $\sum a_i = OP$ (overlap population) is a non-electrostatic metal-ligand contribution to molecular bonding, and $\sum a_{ij} = \sum BQ_iQ_j / d_{ij}\varepsilon$ is a sum of each pairwise electrostatic interaction. Here, d_{ij} is the distance between moieties *i* and *j*; Q_i and Q_j are their effective charges; ε is a dielectric constant, and *B* is an independent constant. ΔS of eq. (3) is a change in the entropy term. Q_i and *OP* are obtained as a result of the Mulliken population analysis of the electronic structures of the complexes on the right- and left-hand side of reaction (2) calculated using the fully relativistic Density Functional Method (DFT) [5].

Geometry and bond lengths (R_e) of $M(H_2O)_8^{4+}$ (D_{2d} -symmetry) and MF_6^{2-} (M = Zr, Hf, and Rf) were assumed on the basis of analysis of the structural data for Zr and Hf and from calculated R_e for some simpler Rf gas-phase compounds [6].

As a result of the calculations, energetic, as well as electronic density distribution parameters were obtained. The Q_M and OP values (Table 1) show an increase in covalence of each type of complexes from Zr to Rf.

Table 1. E^{C} , ΔE^{C} (in eV) and ΔOP for the complexation reaction $M(H_2O)_8^{4+} \Leftrightarrow MF_6^{2-}$

E^{C}	Zr	Hf	Rf
$Q_M: M(H_2O)_8^{4+}$	1.97	1.89	1.85
Q_{M} : MF ₆ ²⁻	0.94	0.85	0.75
E^{C} : M(H ₂ O) ₈ ⁴⁺	-53.34	-52.07	-50.92
$E^{C}: {\rm MF_{6}}^{2-}$	-2.60	-1.18	0.23
ΔE^{C}	50.75	50.88	51.15
OP: $M(H_2O)_8^{4+}$	8.93	9.03	9.11
OP: MF_6^{2-}	2.11	2.38	2.49
⊿OP	-6.82	-6.65	-6.62

The calculated E^C , ΔE^C and ΔOP , are also shown in Table 1. ΔE^C being the predominant type of the metal-ligand interaction shows that Rf should form complexes similarly to those of Zr and Hf only at slightly higher HF concentrations, so that the sequence in the complex formation is Zr > Hf > Rf. Thus, Rf is expected to be extracted by AIX shortly after Hf, with the differences between the three elements being very small.

The theoretically obtained sequence for Zr and Hf is in agreement with the experimental sequence for the descending K_d values in the sorption by CIX and the rising K_d values in the sorption by AIX. It is also in agreement with the descending K_d values for Rf in relation to those of Zr and Hf in the CIX sorption. Taking into account the very small difference in $\Delta G'$ for the complexes of Rf as compared to those of Zr and Hf, the absence of a rising K_d curve on AIX for Rf at higher HF concentrations cannot be explained by the complexation step, provided the same types of complexes are formed. It can, at best, be accounted for by the formation of different types of complexes and their different partition. As a plausible explanation, formation of the neutral H₂RfF₆ in HF/0.1 M HNO₃ could be suggested due to a probable preference of the RfF₆²⁻ complex for the protonation. Nevertheless, from the point of view of the electronic structure of the Rf complexes, it is hard to foresee a large difference between Zr and Hf on the one hand, and Rf on the other hand, whatever is the process. The hypothesis suggested here, as well as those discussed in ref. [2], will be considered in our further theoretical research.

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GAS CHEMICAL INVESTIGATION OF BOHRIUM (Bh, ELEMENT 107)

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Neutron-rich isotopes of Bh can be produced in the nuclear fusion reaction ${}^{249}Bk({}^{22}Ne;4n){}^{267}Bh$. The half-life of ~17 s and the production cross section of about 50 pb, which have been determined during the discovery experiment in Berkeley [1], make ²⁶⁷Bh an ideal candidate to be used for gas phase chemical studies.

Assuming Bh to be a member of group 7 in the periodic table, a suitable chemical isolation procedure was developed in several model experiments using various nuclides of Tc and Re [2,3,4]. The gas chemical separation of MO_3Cl (M = Tc, Re) was shown to be suitable for the study of short-lived isotopes of group 7 elements.

A 670 µg/cm² ²⁴⁹Bk target, prepared by LBNL, was irradiated at the PSI Philips cyclotron with a total beam dose of $3.02*10^{18}$ ²²Ne⁶⁺ particles at a beam energy of 119±1 MeV in the target and an average intensity of about 250 pnA for about 4 weeks. The nuclear reaction products were transported to the reaction oven of a low temperature OLGA III set-up using a carbon aerosol gas-jet. Shortly before the reaction oven a reactive gas mixture of HCl and O₂ was added to the gas-jet. At 1000°C the aerosol particles were burned in the reaction oven and the nuclear reaction products were converted to a large variety of oxides, chlorides, and oxychlorides. Subsequently this mixture of chemical products was separated according their adsorption interaction with the stationary quartz phase in the isothermal part of the chromatography set-up. This part was held at three different isothermal temperatures (T_{iso}). Only the most volatile compounds, able to pass the chromatography, were attached to another gas-jet of CsCl aerosol particles suspended in Ar to transport them to the detection system ROMA. For more details regarding the experimental set-up see [4,6].

6 correlated decay chains, attributed to the decay of ²⁶⁷Bh have been observed. At 180°C and 150°C isothermal temperature (Tiso) 4 respectively 2 chains were detected. No Bh was registered at the same experimental sensitivity at 75°C.

The unambiguous identification of Bh after chemical separation allows to conclude that Bh forms a volatile oxychloride compound, presumably BhO₃Cl, and behaves like a typical member of group 7 of the periodic table. In order to evaluate first thermochemical data of bohrium, the relative yields of Bh at the adjusted isothermal temperatures have been calculated applying a careful statistical analysis of the data. The results are shown in Fig. 1 (squares) together with the yield vs. isothermal temperature curves of the corresponding compounds of Tc and Re (circles). Assuming the Bh compound to be BhO₃Cl, and applying a microscopic model of the adsorption process [5], we evaluated the standard adsorption enthalpy of BhO₃Cl on the quartz surface, $\Delta H_{ads}(BhO_3Cl) = -75^{+9}_{-6} \text{ kJ/mol} (68\% \text{ c.i.}) [6].$ Applying a well established empirical correlation between the single atom property ΔH_{ads} and the property of the macroscopic solid state, sublimation enthalpy ΔH_{subl} [7], from the result of our experiment it was possible to evaluate the first thermochemical measure of volatility of a Bh compound ΔH_{subl} $(BhO_3Cl) = 89^{+21}_{-18} \text{ kJ/mol. Thus, the series of the volatility of}$ group 7 oxychlorides MO₃Cl (M=Tc, Re, Bh) on quartz yields the sequence Tc>Re>Bh. This sequence can also be expected from thermochemical stability trends in the periodic table [8] and from an empirical physisorption model [9]. Experimentally this sequence is supported by the fact, that BhO₃Cl was reclustered with CsCl. This is an additional indication that BhO₃Cl is more similar to ReO₃Cl than to TcO₃Cl, since TcO₃Cl could only be reclustered with FeCl₂-aerosol particles [4].



Yield vs. isothermal temperature curves for the oxy-Fig. 1 108 Tc (t_{1/2}=5.2 s), ¹⁶⁹Re chlorides of $(t_{1/2}=16 \text{ s}),$ and ^{267}Bh (t_{1/2}=17 s). Symbols \rightarrow Experimental data with 1 σ -error bars; Lines \rightarrow Monte Carlo model; thin lines $\rightarrow 1\sigma$ -error range for BhO₃Cl.

Acknowledgments

We are indebted to the US DOE for making the ²⁴⁹Bk target material available through the transplutonium element program at Oak Ridge National Laboratory. We thank the staff of the PSI Philips cyclotron for providing intense beams of ²²Ne. This work was supported by the Swiss National Science Foundation. References

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DEPOSITION AND DETECTION OF VOLATILE OXIDES ON METALLIC

SURFACES WITH CALLISTO

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So far, no chemical properties of element 108, Hassium, are known. It can be assumed, that Hs has similar properties like the homologous elements ruthenium and osmium, i.e., that Hs forms a volatile tetroxide.

To form volatile oxides in-situ, nuclear reaction products are slowed down in oxygen containing gas mixtures, which transport these products. They are deposited and detected with **CALLISTO** (*C*ontinuously Working *A*rrangement For *Cl*uster*l*ess Transport Of *In-situ* Produced Volatile *O*xides) [1].

For the detection of α -active nuclides, a detector phalanx, as shown in Fig. 1, was developed. On one side, ten (10x10) mm² PIN diodes are linearly arranged. On the opposite side, a stripe of metallic Na was placed at a small distance. The carrier gas flows above the Na surface, where volatile oxides deposit and their α -decay can be detected.



Fig. 1

The deposition efficiency of the volatile oxides depends on various factors, e.g., the deposition of OsO_4 on Na decreases considerably with increasing gas flow and it increases with decreasing humidity of the gases, see Fig. 2.



 172,173 Os, formed in a 26 Mg + 152 Gd test-reaction, are unambiguously identified in the α -spectrum, see Fig. 3. Additional smaller peaks can be assigned to other Osisotopes.



In a test experiment, a good Po separation was achieved. After 50 min measuring time, no polonium, formed with a U-target, could be detected in the α -spectrum. With a He/KCl-cluster jet, however, Po was transported and measured in the detection system ROMA [2].

 OsO_4 , as a volatile compound, can be deposited at low temperatures on quartz surfaces. This technique requires much less humid gases than normally supplied, which contain approximately 100-500 ppm water.

Our recently developed gas-drying unit allows reducing the humidity to about 2 ppm. However, still a "collar" of ice deposits inside the cooled quartz spiral beginning at -70 °C. Presently, it is not clear, whether in our experiments OsO_4 was deposited on quartz or on ice. The experimentally observed absolute yield of OsO_4 as a function of temperature is shown in Fig. 4.

Further investigations will require humidity levels below 2 ppm H_2O , which can be obtained from a more efficient gas drying-unit.



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Electronic Structure and Volatility of Group-8 Oxides MO₄, where M = Ru, Os, and Element 108, Hs

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The discovery [1] of a relatively long-lived isotope of element 108, Hs, makes it now possible to design chemical experiments studying its chemical properties. Hs is expected to be a member of group 8 of the Periodic Table and, thus, a homolog of Ru and Os. If the chemical properties of Hs are comparable to those of Ru and Os, it should form a very volatile tetroxide, HsO₄. Several experimental groups including one from Mainz/GSI are, therefore, preparing gas-phase experiments on studying volatility of OsO_4 and its holomogs, RuO₄ and OsO_4 .

In the current report, we present results of the fully relativistic electronic structure calculations for group 8 gasphase tetroxides, RuO_4 , OsO_4 , and HsO_4 , and predict their volatility as an adsorption enthalpy with respect to the particular experimental conditions. The electronic structure calculations of MO_4 (M = Ru, Os, and Hs) including the geometry optimization were performed using the fully relativistic *ab initio* Density-Functional method in the GGA approximation for the exchange-correlation potential [2]. The calculated bond lengths, bond strengths, effective charges and covalence effects (OP) of these molecules are shown in Table 1. They indicate that HsO₄ is the most stable and the most covalent compound in the row.

The adsorption enthalpy of MO_4 on the quartz surface of the chromatography column was calculated using the following model of a molecule-slab interaction

$$E(x)_{\text{molecule-slab}} = -(\pi/6)NC_l/x^3, \tag{1}$$

where N is the number of atoms per cm^3 and x is the moleculesurface interaction distance. In the case of the dispersion interaction of a polarizable molecule with an inert surface consisting of molecular units

$$C_{1} = \frac{3}{2} \frac{\alpha_{1} \alpha_{2}}{\left(\frac{1}{h \nu_{1}} + \frac{1}{h \nu_{2}}\right)}$$
(2)

where hv_1 and hv_2 denote roughly ionization energies, and α_1 and α_2 - polarizabilities of the molecule (1) and the surface (2), respectively. Using the relation between polarizability of the surface and its dielectric constant, eqs. (1) and (2) transform into

$$E(x) = -\frac{3}{16} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{mol}}{\left(\frac{1}{hv_{slab}} + \frac{1}{hv_{mol}} \right) x^3}$$
(3)

where $\varepsilon = 3.81$ is taken for the highest quartz modification - glass.

Table 1. Calculated bond lengths R_e (in Å), bond strengths D_e (in eV), ionization potentials IP (in eV), polarizabilities α (in a.u.), effective charges Q_M and overlap populations (OP) of MO₄ (M = Ru, Os, and Hs)

rtu, 05, und 115)			
Property	RuO_4	OsO_4	HsO ₄
R_e (calc.)	1.73	1.75	1.81
R_{e} (exp.) [3]	1.706	1.711	-
D_e (calc.)	27.48	27.71	28.44
α (calc.)	43.73	40.22	42.24
IP (calc.)	12.25	12.35	12.28
IP (exp.) [4]	12.19	12.35	-
Q_M	1.45	1.46	1.39
OP	1.92	1.94	2.17

By putting the experimental, when available, or calculated parameters into eq. (3), interaction energies E(x) were calculated as shown in Table 2. In the case when the SiO₂ surface is covered with adsorbed O₂, or has an effective charge (*Q*=-0.4), models similar to that of eqs. (1-3) were used giving the interaction energies listed in Table 2 as well.

Table 2. Contributions to the interaction energies E(x) between the neutral MO₄ (M = Ru, Os, and Hs) molecules and a) pure quartz surface; b) surface covered with O₂; c) surface with effective charge Qe (Q = -0.4)

Molecule	$\frac{\alpha - \alpha(\text{SiO}_2)}{E10^{24} x^3}$ (eV cm ³)	$\begin{array}{c} \alpha - \alpha(O_2) \\ E 10^{24} x^3 \\ (eV \text{ cm}^3) \end{array}$	α -Qe E10 ³² x ⁴ (eV cm ⁴)
RuO ₄	4.73	6.28	10.01
OsO_4 HsO ₄	4.48 4.64	6.01 6.16	9.41 9.73

The unknown distance *x* (of 2.25 Å for OsO₄ in the case "a") was deduced from the experimental $\Delta H_{ads}(OsO_4)$ by setting *E*(*x*) equal to -38 ± 1.5 kJ/mol. Taking *x*=2.25 Å as a benchmark and assuming that the molecule-surface distance is directly related to the size of the interacting molecules, the adsorption enthalpies for RuO₄ and HsO₄ were calculated using the data of Table 2. The obtained ΔH_{ads} for RuO₄ and HsO₄ (independently of the model) are larger and smaller than $\Delta H_{ads}(OsO_4)$ by about 2 kJ/mol, respectively. Thus, the volatility has the trend RuO₄ < OsO₄ < HsO₄, with the differences between the species being almost within the experimental uncertainties.

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Ionization potentials of neutral and ionized species of elements 107 and 108 from extended MCDF calculations

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Theoretical predictions of the chemical behaviour of superheavy elements are very important for extensive and sophisticated "one-atom-at-a-time" chemical experiments. A number of experiments have been performed so far up to element 106 and recently a first experiment has been done for element 107. An important first step is the knowledge of the atomic data for each of these elements. (A review on this subject is given in Ref. [1] and [2])

Here we report on the very first large scale Multiconfiguration Dirac–Fock (MCDF) calculations on the elements 107 and 108 in neutral as well as ionized states up to 8+.

The actual calculations which we have performed here are extended relativistic Multiconfiguration Dirac–Fock calculations [3] using up to 650 configuration state functions. The method itself is best described by Grant [4] and Grant and Quiney [5].

Our calculations include all possible configurations which can be constructed from the relativistic ns, $np_{1/2}$, $np_{3/2}$, $(n-1)d_{3/2}$, and $(n-1)d_{5/2}$ single particle wavefunctions for a specific total angular momentum, parity, and charge state. Our assumption is that the core of each element is kept complete and the remaining electrons are distributed in all possible ways in the single particle wavefunctions given above.

Transition	Mı	n	Tc	
	MCDF	Exp.	MCDF	Exp.
$0 + \rightarrow 1 +$	6.84	7.43	6.33	7.28
$0+\rightarrow 2+$	21.7	23.1	20.6	22.54
$0+\rightarrow 3+$	54.2	56.8	49.3	52.08
$0+\rightarrow 4+$	104.4	108	90.9	
$0+\rightarrow 5+$	175.8	180	147.3	
$0+\rightarrow 6+$	270.5	275	219.5	
$0+\rightarrow7+$	388.7	394	307.4	
	Re		Bh	
Transition	Re	9	E	Bh
Transition	Re MCDF	e Exp.	E MCDF	Bh Extrap.
$\begin{array}{c} \text{Transition} \\ 0 + \rightarrow 1 + \end{array}$	Re MCDF 6.84	Exp. 7.46	MCDF 6.82	Bh Extrap. 7.5
$\begin{array}{c} \text{Transition} \\ 0 + \rightarrow 1 + \\ 0 + \rightarrow 2 + \end{array}$	Re MCDF 6.84 22.4	Exp. 7.46 25.53	E MCDF 6.82 23.4	Bh Extrap. 7.5 25.5
$\begin{array}{c} \text{Transition} \\ 0 + \rightarrow 1 + \\ 0 + \rightarrow 2 + \\ 0 + \rightarrow 3 + \end{array}$	Re MCDF 6.84 22.4 48.9	Exp. 7.46 25.53 56.58	E MCDF 6.82 23.4 49.0	3h Extrap. 7.5 25.5 53.4
$\begin{array}{c} \text{Transition} \\ 0 + \rightarrow 1 + \\ 0 + \rightarrow 2 + \\ 0 + \rightarrow 3 + \\ 0 + \rightarrow 4 + \end{array}$	Re MCDF 6.84 22.4 48.9 87.9	Exp. 7.46 25.53 56.58	E MCDF 6.82 23.4 49.0 85.3	Bh Extrap. 7.5 25.5 53.4 89.0
Transition $0+\rightarrow 1+$ $0+\rightarrow 2+$ $0+\rightarrow 3+$ $0+\rightarrow 4+$ $0+\rightarrow 5+$	Re MCDF 6.84 22.4 48.9 87.9 140.4	Exp. 7.46 25.53 56.58	E MCDF 6.82 23.4 49.0 85.3 133.3	Bh Extrap. 7.5 25.5 53.4 89.0 137.5
$\begin{array}{c} \text{Transition} \\ \hline 0+\rightarrow 1+ \\ 0+\rightarrow 2+ \\ 0+\rightarrow 3+ \\ 0+\rightarrow 4+ \\ 0+\rightarrow 5+ \\ 0+\rightarrow 6+ \end{array}$	Re MCDF 6.84 22.4 48.9 87.9 140.4 207.6	Exp. 7.46 25.53 56.58	E MCDF 6.82 23.4 49.0 85.3 133.3 194.5	Bh Extrap. 7.5 25.5 53.4 89.0 137.5 199.0

Table 1: Multiple ionization potentials for group 7 elements in eV.

Due to some differences between the calculated (for the elements 104 to 106 see Ref. [6-8]) and experimental values of the ionization potentials, we have to "correct" the former for the elements 107 and 108 using an extrapolation procedure described in Ref. [6]. In this report we use in addition a double difference extrapolation scheme within

the chemical rows 4 to 6 in order to get reliable values for the row 7 elements.

Our final results are summarized in the two Tables. For each element and all ionization states the theoretical MCDF results from these calculations are presented as well as the experimental values as far as they are known [9]. As can be seen easily the differences per ionization stage are in the order of 1 eV. This fact was used in the extrapolation schemes in the earlier publications of the analogue result for the elements 104 to 106. Using the extrapolation schemes which are discussed in Ref. [6] in detail we arrive at the values which are listed in both Tables for the elements Bh and Hs.

Transition	Fe)	F	łu
	MCDF	Exp.	MCDF	Exp.
$0+\rightarrow 1+$	7.20	7.90	6.36	7.36
$0+\rightarrow 2+$	23.6	24.1	20.9	24.1
$0+\rightarrow 3+$	50.8	54.7	47.5	52.6
$0+\rightarrow 4+$	104.5	109.5	92.3	
$0+\rightarrow 5+$	178.7	184.5	151.6	
$0+\rightarrow 6+$	276.9	283.6	227.3	
$0+\rightarrow7+$	401	409	320	
$0+\rightarrow 8+$			430	
	Os			
Transition	Os	5	H	Is
Transition	Os MCDF	s Exp.	H MCDF	Is Extrap.
$\begin{tabular}{ c c c c c }\hline Transition \\\hline 0+\rightarrow 1+ \end{tabular}$	Os MCDF 7.45	5 Exp. 8.43	H MCDF 6.69	Is Extrap. 7.7
$ \begin{array}{c} \text{Transition} \\ 0+\rightarrow 1+ \\ 0+\rightarrow 2+ \end{array} $	Os MCDF 7.45 23.2	5 Exp. 8.43	H MCDF 6.69 23.3	Is Extrap. 7.7 26
$\begin{tabular}{ c c c c }\hline Transition \\ \hline 0+\rightarrow 1+ \\ 0+\rightarrow 2+ \\ 0+\rightarrow 3+ \\ \hline \end{array}$	Os MCDF 7.45 23.2 48.7	5 Exp. 8.43	H MCDF 6.69 23.3 50.4	Is Extrap. 7.7 26 54
$\begin{tabular}{ c c c c }\hline Transition \\ \hline 0+\rightarrow 1+ \\ 0+\rightarrow 2+ \\ 0+\rightarrow 3+ \\ 0+\rightarrow 4+ \end{tabular}$	Os MCDF 7.45 23.2 48.7 89.7	5 Exp. 8.43	H MCDF 6.69 23.3 50.4 87.0	Is Extrap. 7.7 26 54 92
$\begin{tabular}{ c c c c }\hline \hline Transition \\\hline 0+{\rightarrow}1+\\ 0+{\rightarrow}2+\\ 0+{\rightarrow}3+\\ 0+{\rightarrow}4+\\ 0+{\rightarrow}5+\\\hline \end{tabular}$	Os MCDF 7.45 23.2 48.7 89.7 144.5	5 Exp. 8.43	H MCDF 6.69 23.3 50.4 87.0 137.4	Is Extrap. 7.7 26 54 92 142
$\begin{tabular}{ c c c c }\hline Transition \\\hline 0+\rightarrow 1+ \\0+\rightarrow 2+ \\0+\rightarrow 3+ \\0+\rightarrow 4+ \\0+\rightarrow 5+ \\0+\rightarrow 6+ \end{tabular}$	Os MCDF 7.45 23.2 48.7 89.7 144.5 214.2	5 Exp. 8.43	H MCDF 6.69 23.3 50.4 87.0 137.4 200.5	Is Extrap. 7.7 26 54 92 142 206
$\begin{tabular}{ c c c c }\hline \hline Transition \\\hline 0+\rightarrow 1+ \\0+\rightarrow 2+ \\0+\rightarrow 3+ \\0+\rightarrow 4+ \\0+\rightarrow 5+ \\0+\rightarrow 5+ \\0+\rightarrow 6+ \\0+\rightarrow 7+ \end{tabular}$	Os MCDF 7.45 23.2 48.7 89.7 144.5 214.2 300	5 Exp. 8.43	$\begin{array}{r} & \text{H} \\ \hline \text{MCDF} \\ \hline 6.69 \\ 23.3 \\ 50.4 \\ 87.0 \\ 137.4 \\ 200.5 \\ 278 \end{array}$	Is Extrap. 7.7 26 54 92 142 206

Table 2: Multiple ionization potentials for group 8 elements in eV.

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Adsorption Studies with Homologs of Superheavy Elements

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Introduction

In preparation of chemical studies with superheavy elements around Z = 114, the adsorption behavior of these elements and their lighter homologs on different metals has been predicted based on (semi-)empirical models and extrapolations (see e.g. [1, 2]).

Adsorption studies with SHE homologs were performed on various metals, especially metals of group 10 and 11 (see e.g. [3]). The experimental results mainly confirmed the calculated data, but in a few cases great differences between predicted and experimental data were observed. Therefore, the adsorption behavior of SHE homologs on further metals is of great interest to prove the validity of the predictions.

In the present work the adsorption of Tl, Pb, Bi, and Po on the group 5 metals V, Nb, Ta as well as on Mo, Ni, Ti has been studied by thermochromatography. Experimental data have been compared to predictions.

Experimental

Bi, Pb, and Tl isotopes were produced by bombarding an ^{nat}Ir target (0.3 mg/cm²) with a ¹²C beam (90 MeV on target) at the GSI UNILAC. The recoil nuclei of the nuclear reactions were caught in catcher foils made of 9 μ m Cu. These foils were preconditioned by heating them up to 800°C for 15 min in a 100 mL/min gas flow of N₂/H₂ (ratio 90:10). Hydrogen was used to reduce the surface layer of Cu oxide to Cu. The catcher foils served as the thermochromatographic samples without further preparation.

preparation. ²¹⁰Po was obtained by neutron activation of ^{nat}Bi at the TRIGA Mainz reactor and subsequent decay of the produced ²¹⁰Bi. Po was separated from Bi by thermochromatography according to [4] and deposited on a Ta column. One cm pieces of the Ta column with the adsorbed Po were used as samples for the thermochromatography experiments.

The experimental setup was similar to that described in detail in [5]. Thermochromatographic columns were made from 20 - 25 μ m thick Ti, V, Nb, Ta, Mo, and Ni foils. Quartz glass columns served as support tubes. The inside of these tubes was lined with thin Ta foils in order to adsorb the oxygen emitted from the quartz glass at high temperatures. A carrier gas flow of 25 or 50 mL/min He was established. The starting temperature was varied between 700 and 950°C. After 15 or 30 min thermochromatography time the nuclide distribution along the column was determined by γ - or α -spectroscopy of 1 cm column pieces.

Results

Po was nearly completely (> 98 %) volatilized from the Ta foils. Tl, Pb, and Bi partly remained in the catcher foils.

Thermochemical data were determined by two methods:

- (1) Adsorption entropy and enthalpy were calculated according to [6] with $\tau_0 = 10^{-12}$ s.
- (2) ΔS_{ads}° and ΔH_{ads}° were determined according to [7] using an individual τ_0 for each adsorpt-adsorbent combination.

As an example, predicted and experimentally determined adsorption enthalpies for Tl on several adsorbent metals are depicted in Fig. 1.





The main results of our adsorption studies can be summarized as follows:

- Irrespective of the used method, significantly less negative adsorption enthalpies were obtained than predicted by [1].
- Our results correspond quite well with the experimental data given in [3].
- As predicted, less negative or similar adsorption enthalpies were found for all studied elements on Nb compared to Ni, Ta, and Ti. However, the least negative adsorption enthalpies of all studied elements were surprisingly obtained on Mo. This might be an erroneous result caused by an oxide layer on the column surface which could not be removed by heating in a He flow.
- On titanium, Tl and Pb were deposited in the starting position and only an upper limit of ΔH_{ads}° can be given. On all other adsorbent metals, less negative adsorption enthalpies were obtained for Tl than for Pb.

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A Geometric Model for Direct Condensation

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Direct condensation has been established as a well-suited deposition mode for high temperature gas chromatography experiments. Unfortunately, there is no simple model of this process in the literature until now. The model proposed here neglects the exact flow pattern near the deposition foil as well as diffusion processes which might influence the yield. A flow pattern of an underexpanded supersonic jet is formed during the efflux of the reaction gas into a low pressure region, e.g. the ROMA device. Such jets are characterized by a shock cell, the so-called zone of silence, in which the flow velocity is much greater than the local speed of sound and a boundary region between the jet and the ambient gas, in which the gas moves slightly faster than at the exit [1, 2]. The zone of silence consists of a barrel-shaped shock surrounding the jet and a nearly planar normal shock, or Mach disk, downstream. Pressure and temperature decrease dramatically in the zone of silence, whereas the mass flow rate is nearly unchanged. Behind the Mach disk the flow velocity drops down to a subsonic flow. Good conditions for direct condensation of chemical compounds exist within the zone of silence.

The radius of the Mach disk is

$$r_{mach} = \frac{0.67 \text{ bar} \cdot r_{in}}{\sqrt{P_0 P_{ROMA}}}$$

and its distance from the outlet is $d_{mach} = 4 r_{mach}$



Fig. 1: Geometric model for the evaluation of the deposition yield (symbols are explained below)

A simple geometrical model (Fig. 1) is used to estimate the deposition yield. This model is based on four assumptions:

1) The gas velocity v_{\parallel} in the direction of the axis of the chromatography column after passing the end of the column is constant. 2) The flow pattern is a sharp cone. The axis of the cone has the same direction as the axis of the chromatography column; the cone has an opening angle of $2\vartheta_{max}$. 3) The gas density in a disk perpendicular to the axis of the flow cone is constant. 4) The gas flow perpendicular to the axis of the cone has a constant velocity.

The yield ϵ is defined by $\epsilon = \frac{\dot{m}_{coll}}{\dot{m}_{out}}$. The mass flow rates

 \dot{m}_{coll} and \dot{m}_{out} can be calculated by integrating the local gas density $\rho(d)$ over the collection and the outlet cross section, respectively.

$$\begin{split} \text{This leads to} \qquad \dot{m}_{_{out}} = \pi \ r_{_{in}}^{_{in}} \ v_{_{\parallel}} \ \rho_{_{L}} \\ \dot{m}_{_{coll}} = \int\limits_{0}^{_{tot}} 2\pi \ r \ v_{_{\parallel}} \ \rho(d) \ dr \end{split}$$

The mass flow rate is constant. $\rho(d)$ can be calculated by

$$\rho(d) = \left(\frac{r_{out}}{r(d)}\right)^2 \rho_L$$

The exit velocity v_{\parallel} of the gas for $P_{ROMA} < P_0$ is given by

$$v_{\parallel} = \sqrt{\kappa \frac{P_{\rm L}}{\rho_{\rm L}}}$$

and the velocity component $v_{\!\perp}$ perpendicular to the direction of the out flow can be calculated by

$$v_{\perp} = \sqrt{\frac{2\kappa}{\kappa - 1}} \cdot \frac{P_{L}}{\rho_{L}} \cdot \left[1 - \left(\frac{P_{ROMA}}{P_{L}}\right)^{\frac{\kappa - 1}{\kappa}} \right]$$

The opening angle ϑ_{max} of the flow cone can be calculated by

$$\tan\left(\vartheta_{\max}\right) = \frac{\mathbf{v}_{\perp}}{\mathbf{v}_{\parallel}}$$

Combining these formulas yields

$$\dot{m}_{coll} = \begin{cases} \pi & r_{in}^2 & v_{\parallel} & \rho_L & \text{for} & r\left(d\right) < r_{coll} \\ \pi & \left(\frac{r_{coll}}{r\left(d\right)}\right)^2 & r_{in}^2 & v_{\parallel} & \rho_L & \text{for} & r\left(d\right) > r_{coll} \end{cases}$$

for the collected mass flow.

Finally, the yield ε can be obtained by

$$\varepsilon = \begin{cases} \frac{\kappa - 1}{2} \cdot \left(\frac{r_{\text{coll}}}{d}\right)^2 \cdot \left[1 - \left(\frac{P_{\text{ROMA}}}{P_L}\right)^{\frac{\kappa - 1}{\kappa}}\right]^{-1} & \text{for } r(d) > r_{\text{coll}} \\ 1 & \text{for } r(d) < r_{\text{coll}} \end{cases}$$

Experimental data (ϵ , optimum d, spot diameter) could be reproduced well with the proposed geometrical model [3]. For instance, the spots observed experimentally at the pressure optimum can be explained by the zone of silence. The Mach disk has a diameter of 3.3 mm close to the observed diameter of about 3 mm.

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Symbols: $m_{coll} = mass$ collected on the catcher foil, $m_{out} = mass$ flowing out of the tip of the chromatography column (cc), $r_{in} = inner$ radius at the end of the cc, $\rho(d) = density$ at the distance d from the outlet, $r_{coll} = radius$ of the catcher foil, d = distance between cc and catcher foil, r(d) = radius of the cone = $d tan(\vartheta_{max})$, $\kappa = POISSON$ coefficient = C_p / C_v , $P_0 = back$ pressure in the cc, $P_{ROMA} = ambient$ pressure in the ROMA device, $\rho_0 = gas$ density at P_0 , $P_L = P_{radius}$

Laval pressure =
$$P_0\left(\frac{2}{\kappa+1}\right)^{\frac{\kappa}{\kappa-1}}$$
, ρ_L = Laval density = $\rho_0\left(\frac{2}{\kappa+1}\right)^{\frac{1}{\kappa-1}}$

