Preliminary Results of an Experiment to Investigate the Chemical Properties of Bohrium (Bh, element 107)

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Between August 20th and September 26th a 670 µg/cm^2 ^{249}Bk target, prepared by LBNL, was irradiated with a total beam dose of $3.02*10^{18}$ ^{22}Ne^{6+} particles at a beam energy of 118 MeV and an average intensity of about 250 pnA at PSI Philips cyclotron in order to produce the nuclide ^{267}Bh in the reaction ^{249}Bk(^{22}Ne; 4n)^{267}Bh. The recoiling reaction products were thermalised and transported with a 1 l/min He/C-aerosol gas-jet to the reaction oven of the 3 m distant remotely controlled low temperature OLGA III set-up [1]. A reactive gas mixture of 50 ml/min HCl and 50 ml/min O_2 was added in order to oxidise the C-aerosols and to form oxychloride compounds. Volatile compounds were separated from less volatile compounds in the adjoining isothermal section (1.5 m legth, 1.5 mm i.d.) of the quartz chromatography column depending on their adsorption behaviour and half-life of the nuclide. This section was kept at three different isothermal temperatures (Tab.1, T_{iso}). After passing the column the isolated products were reattached to a 1 l/min He/CsCl gas-jet in the recluster chamber and transported to the ROtating wheel Multidetector Analyser (ROMA). The aerosol particles were impacted in vacuum (~5 mbar) on thin (30-40 µg/cm^2) polyethylene foils, which were mounted on the circumference of the wheel. The stepping time was 10 s. Each of the collected 178000 samples was then measured between 12 pairs of PIPS-detectors for α- and sf-decays. Since the target contained 100 µg/cm^2 ^{159}Tb, ^{176}Re was also produced, serving as a yield monitor for the chemical separation. The overall yield of the whole separation process - from thermalisation of the recoiling ^{176}Re to the collection of the CsCl aerosols in the ROMA set-up was determined to be about 16%. The detection efficiency for an α- or sf-decay was about 70%.

A total of 6 correlated decay chains attributed to the decay of ^{267}Bh were observed and listed in Tab.1 together with the evaluated number of expected random events (N_R).
At 180°C and 150°C isothermal temperature (T_{iso}) 4 respectively 2 events were detected. At 75°C no event was registered. The unambiguous identification of Bh after chemical separation allows to conclude that Bh like its lighter homologues forms a volatile oxychloride compound, presumably BhO_3Cl and behaves like a typical member of group 7 of the Periodic Table.
Assuming the Bh compound to be BhO_3Cl and applying a microscopic model of the adsorption process developed by Zvara [2], we evaluated the standard adsorption enthalpy of BhO_3Cl on the quartz surface, $\Delta H_{ads}(BhO_3Cl) = -77^{+10}_{-8}$ kJ/mol.
The series of the adsorption enthalpies of group 7 oxychlorides MO_3Cl (M=Tc, Re, Bh) on quartz yields the sequence Tc>Re>Bh. This sequence can also be expected from classical stability trends in the Periodic Table.
In our experiment BhO_3Cl was reclustered with CsCl. This is an additional indication that BhO_3Cl is more similar to ReO_3Cl than to TcO_3Cl, since TcO_3Cl could only be reclustered with $FeCl_2$-aerosol particles and not with CsCl. [3].

Acknowledgments

T_{iso} [°C]	Beam dose: ^{22}Ne^{6+}	Decay chain	$E_{\alpha1}$ [MeV]	t_1 [s]	$E_{\alpha2}$ [MeV]	Δt_2 [s]	$E_{\alpha3}$ [MeV]	Δt_3 [s]	Decay assignment	N_R
180°C	$1.02*10^{18}$	1	8.84	26.7	8.35	73.4			^{267}Bh → ^{263}Db or ^{259}Lr	1.2
		2	8.72	2.9	8.40	29.9			^{267}Bh → ^{263}Db or ^{259}Lr	
		3	8.81	18.4	101 86	16.3			^{267}Bh → ^{263}Db or ^{259}Lr	0.1
		4	8.91	10.5	8.37	0.8	8.41	14.6	^{267}Bh → ^{263}Db → ^{259}Lr	0.001
150°C	$1.00*10^{18}$	5	8.81	24.5	82	21.1			^{267}Bh → ^{263}Db or ^{259}Lr	0.1
		6	8.85	34.4	46	98.9			^{267}Bh → ^{263}Db or ^{259}Lr	
75°C	$1.00*10^{18}$									

Table 1: Correlated decay chains related directly to the decay of ^{267}Bh detected after the chemical separation.

References

[1] R. Eichler et al., PSI-Scient. Rep. 1998, 123 (1999).
[2] I. Zvara, Radiochimica Acta 38, 95 (1982).
[3] R. Eichler et al., PSI Annual report 1999.

Electronic Structure and Volatility of Element 107 (Bh) Oxychloride

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First experiments on the chemical identification of element 107, bohrium, in the gas phase have recently been conducted [1]. They have successfully shown element 107 to form an oxychloride compound in the HCl/O_2 medium, probably of the type MO_3Cl, similar to the lighter homologs in group 7 , Tc and Re. In earlier test thermochromatography experiments [2] on volatility of Re and Tc compounds in the HCl/O_2 medium, the adsorption enthalpies and the boiling points were evaluated as –51 kJ/mol and –61 kJ/mol for TcO_3Cl and ReO_3Cl, respectively. In the current report, we present results of the electronic structure calculations for group 7 gas-phase compounds TcO_3Cl, ReO_3Cl and BhO_3Cl, which were performed as predictions for the 107 experiments, and give estimates of volatility as an adsorption enthalpy with respect to the particular experimental conditions.

The calculations were performed using the fully relativistic *ab initio* Density-Functional method [3]. The frozen core approximation was used and the basis set included valence orbitals of the elements of interest. Mulliken population analysis was utilized for the electronic density distribution. In cases where the geometry was unknown it was assumed based on experimental or extrapolated ionic radii.

As a result, the following properties have been calculated: MO energies, ionization potentials (IP), electronic density distributions, effective charges (Q), overlap populations (OP), dipole moments (μ), and electric dipole polarizabilities (α) (Table 1). They show the closest analogy between the Re and Bh compounds.

Table 1. Effective charges (Q_M), overlap populations (OP), Coulomb part of the binding energy (E^C), dipole moments (μ), electric dipole polarizabilities (α) and ionization potentials (IP) for MO_3Cl (M = Tc, Re and Bh)

Property	TcO_3Cl	ReO_3Cl	BhO_3Cl
Q_M	1.28	1.21	1.13
OP	1.93	2.20	2.31
E^C, eV	-10.03	-9.11	-7.74
μ, D	0.93	1.29	1.95
α, 10^{24} cm³	4.94	5.91	9.46
IP, eV	10.74	12.39	12.86

By using the calculated values and supposing that the interaction of the molecules with the SiO_2 surface takes place via the Cl atoms (with the charge Ze) adsorbed on it, the energies of the following three types of the molecule - ionized surface interaction have been calculated:

1) Molecular dipole - charge (Ze)

$$\varepsilon(\mu, Ze) = -2\mu Ze/x^2,$$

2) Molecular polarizability - charge (Ze)

$$\varepsilon(\alpha, Ze) = -Z^2 e^2 \alpha/2x^4$$

3) Dispersion interaction

$$\varepsilon(\alpha, \alpha) = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{x^6 \left(\frac{1}{h\nu_1} + \frac{1}{h\nu_2} \right)}$$

Here, $h\nu$ are roughly IP of the molecules and x is the molecule-surface distance. The Cl parameters α and IP have been calculated as a dependence on its realistic effective charge. All the calculated contributions to the interaction energy (for Z = -0.4 which is the most realistic value) are given in Table 2.

Table 2. Contributions to the interaction energies ε between neutral MO_3Cl molecules (M = Tc, Re and Bh) and Cl^Z(surface) (Z = -0.4)

Molecule	μ-Ze $\varepsilon 10^{28}$ x^2 (erg cm²)	α-Ze $\varepsilon 10^{44}$ x^4 (erg cm³)	α-α(Cl) $\varepsilon 10^{60}$ x^6 (erg cm⁶)
TcO_3Cl	3.59	9.12	576.88
ReO_3Cl	4.96	10.91	729.87
BhO_3Cl	7.49	17.46	1186.81

The unknown distance x has been deduced from the measured adsorption enthalpy for ReO_3Cl by setting the expression for the interaction energy $3.1/x^2 + 6.8/x^4 + 455.6/x^6$ (in eV) obtained using the terms from Table 2 to H_{ads} = -61±3 kJ/mol (0.63 eV). This resulted in x = 3.38 Å for ReO_3Cl, which is related to the case when the adsorbate molecule and the Cl ion touch each other. Taking this as a benchmark and assuming that the molecule-surface distance is directly related to the size of the interacting molecules (which means x = 3.37 Å for TcO_3Cl and x = 3.44 Å for BhO_3Cl), we have calculated adsorption enthalpies for the other two oxychlorides using the data of Table 2. Thus, we obtained ΔH_{ads} = -47 kJ/mol and ΔH_{ads} = -88 kJ/mol for TcO_3Cl and BhO_3Cl, respectively. The experimental value of ΔH_{ads} = -51± 3 kJ/mol for TcO_3Cl is indicative of an adequate theoretical description of the process. Thus, the volatility of the group 7 oxychlorides was predicted to change in the following way TcO_3Cl > ReO_3Cl > BhO_3Cl.

References

[1] H. W. Gäggeler, PSI *Pressconference* 15.9.1999
[2] R. Eichler, *et al.*, *Radiochim. Acta* 1999, in print
[3] T. Bastug, *et al.*, *Chem. Phys. Lett.* 211, 119 (1993)

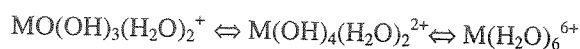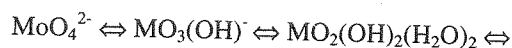# Solution Chemistry of Element 106: Hydrolysis of Group 6 Cations

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The first chemical study of seaborgium in aqueous solution was its one-step elution as a neutral or anionic species in 0.1 M $HNO_3/5\times10^{-4}$ M HF from cation exchange columns [1]. These experiments showed the most stable oxidation state in aqueous solutions to be +6 as expected for a member of group 6 elements. The lighter homologs of Sg, Mo and W, are known to form under these conditions neutral or anionic oxo- or oxofluoro complexes. To exclude the influence of the strong complexing action of the F$^-$ ions, another similar study [2] was performed in which the group 6 elements were eluted from cation exchange columns in 0.1 M HNO_3 without HF. In these later experiments, Sg was not eluted from the column in contrast to W, and this non-tungsten like behavior of Sg was tentatively attributed to its lower tendency to hydrolyze compared to that of tungsten. To render a theoretical assistance to those experiments, we have performed a study of hydrolysis of the group 6 elements using relativistic density-functional *ab initio* calculations of the hydrated and hydrolysed species of Mo, W and Sg.

The free energy changes for the following protonation processes (the reverse of the hydrolysis)

$$MoO_4^{2-} \Leftrightarrow MO_3(OH)^- \Leftrightarrow MO_2(OH)_2(H_2O)_2 \Leftrightarrow$$

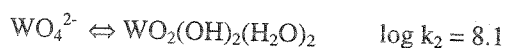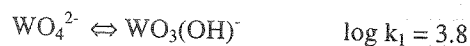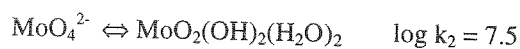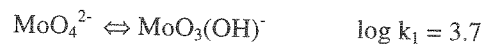$$MO(OH)_3(H_2O)_2^+ \Leftrightarrow M(OH)_4(H_2O)_2^{2+} \Leftrightarrow M(H_2O)_6^{6+}$$

have been defined for Mo, W and Sg. For this purpose, a model has been used [3] which enables determination of the changes in the ionic and covalent contributions to the total binding energy separately using the Mulliken population analysis of the electronic density distribution. The latter was calculated using the fully relativistic *ab initio* Density-Functional method [4]. The geometry of the molecules was assumed based on experimental or extrapolated ionic radii.

As a result of the calculations, the changes in the Coulomb part of the free energy for the protonation processes indicated above are presented in Table 1.

Table 1. Changes in the Coulomb part of the free energy ΔE^C (in eV) for the protonation reactions

Reaction	Mo	W	Sg
$MO_4^{2-} \Leftrightarrow MO_3(OH)^-$	-13.18	-13.22	-13.45
$MO_3(OH)^- \Leftrightarrow MO_2(OH)_2(H_2O)_2$	-20.86	-21.51	-20.92
$MO_2(OH)_2(H_2O)_2 \Leftrightarrow MO(OH)_3(H_2O)_2^+$	-4.96	-5.33	-5.53
$MO(OH)_3(H_2O)_2^+ \Leftrightarrow M(OH)_4(H_2O)_2^{2+}$	-0.61	-0.67	-1.12
$M(OH)_4(H_2O)_2^{2+} \Leftrightarrow M(H_2O)_6^{6+}$	39.87	37.12	34.96

Comparisons of ΔE^C with the experimental equilibrium constants

$$MoO_4^{2-} \Leftrightarrow MoO_3(OH)^- \qquad \log k_1 = 3.7$$

$$MoO_4^{2-} \Leftrightarrow MoO_2(OH)_2(H_2O)_2 \qquad \log k_2 = 7.5$$

$$WO_4^{2-} \Leftrightarrow WO_3(OH)^- \qquad \log k_1 = 3.8$$

$$WO_4^{2-} \Leftrightarrow WO_2(OH)_2(H_2O)_2 \qquad \log k_2 = 8.1$$

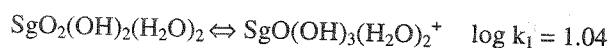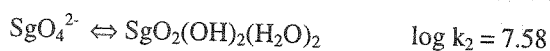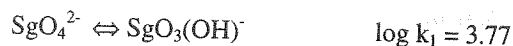have shown the former to correlate with k as it is seen from the following relations

$$\log k_1(Mo)/\Delta E^C_1(Mo)= 3.7/13.18 = 0.28$$

$$\log k_1 (W)/\Delta E^C_1(W) = 3.8/13.22 = 0.28$$

$$\log k_2(Mo)/\Delta E^C_2(Mo)= 7.50/34.01 = 0.22$$

$$\log k_2(W)/\Delta E^C_2(W) = 8.1/34.73 = 0.23$$

and to define trends in the changes in the free energy of the reactions and, hence, in hydrolysis. Using the relations between the k values and ΔE^C, the following equilibrium constants for the Sg reactions have been defined

$$SgO_4^{2-} \Leftrightarrow SgO_3(OH)^- \qquad \log k_1 = 3.77$$

$$SgO_4^{2-} \Leftrightarrow SgO_2(OH)_2(H_2O)_2 \qquad \log k_2 = 7.58$$

$$SgO_2(OH)_2(H_2O)_2 \Leftrightarrow SgO(OH)_3(H_2O)_2^+ \qquad \log k_1 = 1.04$$

Thus, the results of the calculations (Table 1) have shown hydrolysis of the cations in acid solutions with the final formation of the neutral species

$$M(H_2O)_6^{6+} \Leftrightarrow ... \Leftrightarrow MO_2(OH)_2(H_2O)_2$$
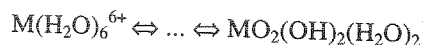
to change in the following way Mo > W > Sg, while for the further hydrolysis in solutions of higher pH

$$MO_2(OH)_2(H_2O)_2 \Leftrightarrow ... \Leftrightarrow MO_4^{2-}$$
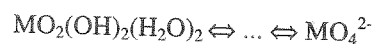
the order is reversed Mo $\geq$ Sg > W. The first predicted sequence of hydrolysis is in full agreement with that obtained experimentally for the acidic solutions with pH=1.

References

[1] M. Schädel, *et al.*, *Nature* **388**, 55 (1997)
[2] M. Schädel, *et al.*, *Radiochim. Acta* **83**, 163 (1998)
[3] V. Pershina, *Radiochim. Acta* **80**, 65 (1998)
[4] T. Bastug *et al.*, *Chem. Phys. Lett.* **211**, 119 (1993)

Another example is the mass determination of very short-lived isotopes like ^{32}Ar and ^{74}Rb. The exact knowledge of the mass of ^{32}Ar makes it possible to improve the constraints on scalar weak interaction [10] while a good knowledge of the mass of ^{74}Rb helps to extend the charge dependent systematics on pure Fermi decays towards higher Z.

The SHIPTRAP Project at GSI

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The investigation of the properties of very heavy elements or of short-lived doubly magic and neighboring nuclei (e.g. ^{100}Sn) is a very important testing ground for the ability of the existing nuclear models to describe stabilization effects of the underlying shell structure.

The aim of the SHIPTRAP project is to provide isobarically pure ion beams of low emittance and low energy. It will allow one to perform ISOL-like experiments on transuranium isotopes or other fusion reaction products, e.g. precise mass measurements, laser spectroscopy or β-spectroscopy. The system is designed to capture radioactive ions from the velocity filter SHIP at GSI and to cool them to room temperature in a volume of some mm^3 with an overall efficiency of greater than 1%.

In the experiment the radioactive ions to be investigated are separated from the primary beam projectiles in the SHIP separator. The energy of the recoil ions is reduced in degrader foils followed by a helium buffer gas cell (p < 1 bar) [11]. ¿From this stopping volume either the remaining singly charged ions or the neutralized and stepwise resonantly laser-ionized ions are extracted by electric fields and a gas flow through a nozzle. From there the ions are captured with high efficiency (> 50%) in two subsequent radiofrequency quadrupole (RFQ) ion guides [12] forming differential pumping stages. The last section of the second ion guide is a RFQ ion trap where the ions are collected and cooled down to an energy of about 0.05 eV.

In 1999, a RFQ was built and tested with stable singly charged ions from an off-line ion source. The characteristics of the buncher, like acceptance of the incoming beam or longitudinal and transverse emittance of the resulting beam have been investigated. According to these tests the design of an optimized RFQ rod structure, the bunching system, has been finished. After the fabrication of the parts of the RFQ rod structure the assembly and testing of this system has started. The optimized buncher will be connected to the other parts of the setup in 2000. After the buncher the ions are extracted into a Penning trap system, which will be similar to the cooler and measurement trap of the ISOLTRAP facility at CERN [8, 9]. In the cooler trap the ions are mass-selectively cooled and isomeric contamination is removed if not already achieved by resonant laser ionization. The purified and cooled ion cloud is ejected as a bunch or as a continuous beam, accelerated and guided to an experimental area where e.g. mass spectrometry, nuclear spectroscopy, high-resolution laser spectroscopy or chemical investigations can be performed. The design of the Penning trap system will be finished in early 2000. After assembly of the parts first tests can be performed with stable singly charged ions from an off-line ion source. It is planned to connect the RFQ ion buncher and the Penning traps to SHIP in the autumn 2000.

The Buffer Gas Cell and the Extraction RFQ for SHIPTRAP

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The design, construction and manufacturing of the test setup of the buffer gas cell and the extraction RFQ for SHIPTRAP is finished after a wide range of simulations. The simulations covered the following topics: stopping of the ions in the buffer gas, drag of the ions via the electric field in the cell towards a supersonic nozzle, drag of the ions through the nozzle with the gas flow, and gas flow parameters in the extraction RFQ; cooling of the ions in the extraction RFQ.

Based on the results of these simulations a prototype gas cell has been constructed which is shown in Fig. 3. After passing through a 565 μg/cm^2 Ni foil the high energy ions are stopped in argon at pressures of 50 to 200 mbar in the center of the gas cell. The electric field geometry in the gas cell is presently created by three electrodes which allow for an extraction with a good focusing of the stopped ions within 10 ms with maximum voltages of 700 V (Fig. 3). Recent simulations have shown that two additional electrodes in the area of the stopped ion cloud can improve the extraction time. To prevent the ion beam defocusing in the supersonic nozzle and to separate the effects of the electrostatic field and the gas flow on the ion beam formation, the nozzle entrance is covered by a high transmission grid at nozzle potential.

The geometry of the supersonic nozzle with a diameter of the throat of 0.6 mm is optimized to drag ions through it

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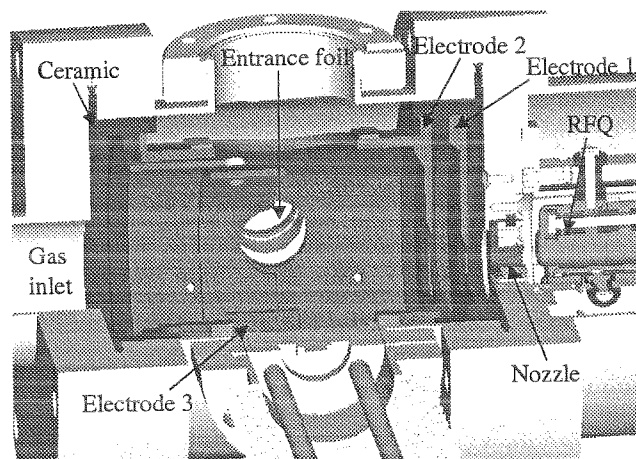Figure 3: The SHIPTRAP buffer gas cell and part of the extraction RFQ.

Kinetic studies of the reactions of Ru+ an Os+ with oxygen in a Penning trap

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[2]Institut für Physik, Johannes Gutenberg-Universität Mainz, D-55099 Mainz

A new method for future experiments on the chemistry of heavy elements is being established, for which the *Mainz Cluster Trap* [1] serves as a model apparatus for SHIPTRAP at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt. Both setups are equiped with a Penning trap to store ions for e.g. chemical reactions.

Ruthenium ions and osmium ions, as homologs of element 108 (hassium, Hs), are produced in a laser-vaporization source and transferred into the Penning trap. Oxides (MO_x^+) formed in the source are radially ejected from the trap, leaving an ensemble of pure Os^+ or Ru^+ cations in an oxygen atmosphere. The ions are stored for a variable reaction time of 10μs to 20s. After the reaction time, the products are extracted into a Time-of-Flight mass spectrometer (TOF). Thus, the buildup of metal-oxid ions can be measured time resolved at various oxygen pressures.

The pressure in the trap region is determined by the reference reaction $Ti^+ + O_2 \rightarrow TiO^+ + O$ [2]. It has been varied between $5*10^{-7}$ mbar and $2*10^{-5}$ mbar.

In the experiments with ruthenium as well as osmium, the following reaction sequence is observed:

$$M^+ \rightarrow MO^+ \rightarrow MO_2^+ \qquad (1)$$
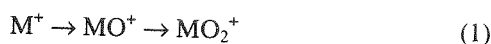
Higher oxidation states are not found at any of the given oxygen pressures. In case of ruthenium, the reaction is very slow and even with a reaction time Δt=20s the yield of RuO_x^+ does not exceed 60%. For osmium, a 100% yield for OsO_2^+ is achieved for reaction times of about Δt=10s.

The rate constants k_1 ($M^+ \rightarrow MO^+$) and k_2 ($MO^+ \rightarrow MO_2^+$) are obtained by fitting exponential functions to a plot of the relative ion signals vs. reaction time.

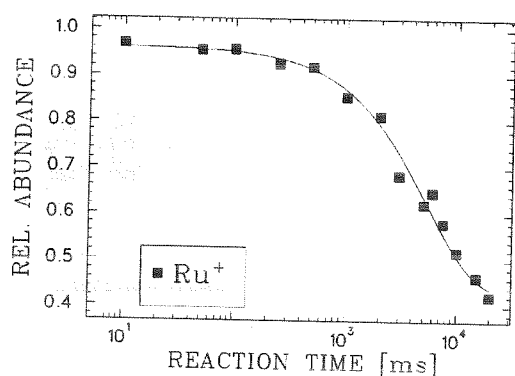Fig.1   Decrease of Ru+ signal

The first rate constant is taken from the decrease of the number of ruthenium or osmium ions (fig.1). The exponential function is shown in equation 2.

$$[M] = A_{0(M)} * e^{-k_1 t} \qquad (2)$$

The second constant can either be taken from the increase of the MO_2^+ signal or from a maximum in the function of the MO^+ vs. time (see fig.2). The latter gives a ratio for the two constants as shown in equation 3.

$$MO_{max} = A_{0(M)} * \left(\frac{k_1}{k_2}\right)^{\frac{1}{1-\frac{k_1}{k_2}}} \qquad (3)$$

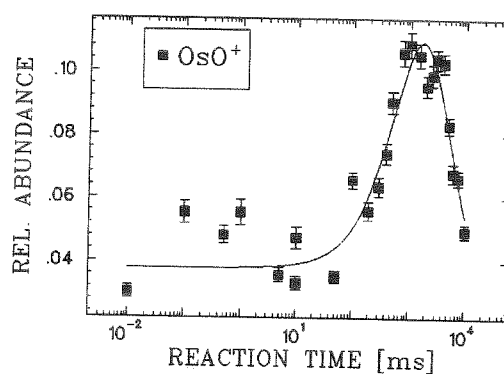In the present experiment, this maximum can only be observed in the case of osmium (fig.2).

Fig.2   OsO+ signal with maximum of 10% abundance

The resulting rate constants for ruthenium and osmium are $k_1=(3.2\pm0.4)*10^{-12}$ $cm^3*molecule^{-1}*s^{-1}$, $k_2=(7.8\pm1.8)*10^{-12}$ $cm^3*molecule^{-1}*s^{-1}$, and $k_1=(7.2\pm0.6)*10^{-12}$ $cm^3*molecule^{-1}*s^{-1}$, $k_2=(57.7\pm4.5)*10^{-12}$ $cm^3*molecule^{-1}*s^{-1}$, respectively. These values seem to be too small to consider an experiment with 10-s ^{269}Hs [3] at similar oxygen pressures.

Thus, a future experiment must be performed at higher oxygen pressures. In addition, dynamical calculations of the transition states as well as molecular orbital calculations of the electronic structure and stability of the ionic species MO^+, MO_2^+, MO_3^+ and MO_4^+ (M = Ru, Os, Hs) are required and in preparation [4] to extrapolate the observed reaction rates of Ru and Os to element 108, Hs.

References

[1] L. Schweikhard, S. Krückeberg, K. Lützenkirchen, C. Walther, *Eur. Phys. J.* **D9**, in print

[2] R. Johnsen, F.R. Castell, M.A. Biondi, *J. Chem. Phys.*, **61**, 5404 (1974)

[3] S. Hofmann, V. Ninov, F.P. Hessberger, P. Armbruster, H. Folger, G. Münzenberg, H.-J. Schött, A.G. Popeko, A.V. Yeremin, S. Saro, R. Janik, M. Leino, Z. Phys. **A354**, 229 (1996)

[4] V. Pershina, private communication

THE IN-SITU SYNTHESIS OF VOLATILE OXIDES OF OSMIUM AND RUTHENIUM WITH CALLISTO

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The chemical properties of element 108, hassium, are not known yet. It is supposed, that it should show a similar chemical behaviour like osmium and ruthenium, because they are all members of group 8.

Osmium and ruthenium are able to form volatile tetroxides. This leads to the conclusion, that hassium may be able to form a stable and volatile tetroxide too. To prepare such an experiment, it is necessary to investigate the on-line production and transport of the tetroxides of ruthenium and osmium.

For that reason, a Continuously Working Arrangement For Clusterless Transport Of In-situ Produced Volatile Oxides, **CALLISTO**, was developed. The volatile oxides can be prepared directly in the target chamber by slowing down the products of the nuclear fusion reaction in a helium-oxygen mixture. Osmium and ruthenium were produced at the UNILAC through bombardment of a ^{nat}Yb-target / ^{nat}Sr-target with a ^{12}C-beam. We found, that a target chamber with a small volume leads to better yields at higher beam intensities (Fig. 1).
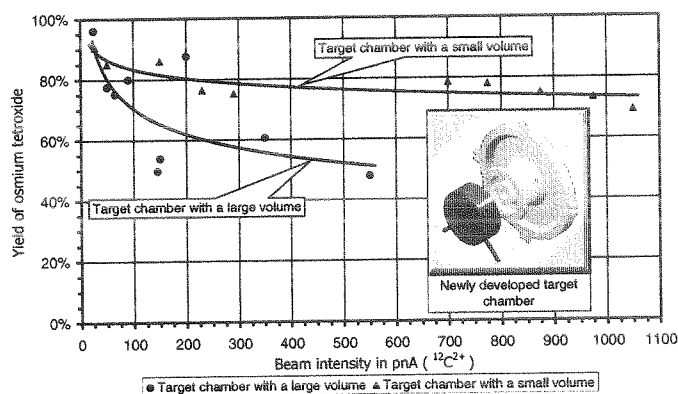
Figure 1: Comparison of different target chambers

To determine the most suitable material for this target chamber, different inserts were tested.

For maximum yield, it is necessary to determine the optimum mixture of helium and oxygen. We found a maximum at 10 ml/min O_2 for osmium and at 75ml/min for ruthenium. This maximum was confirmed at different beam intensities (Fig. 2).
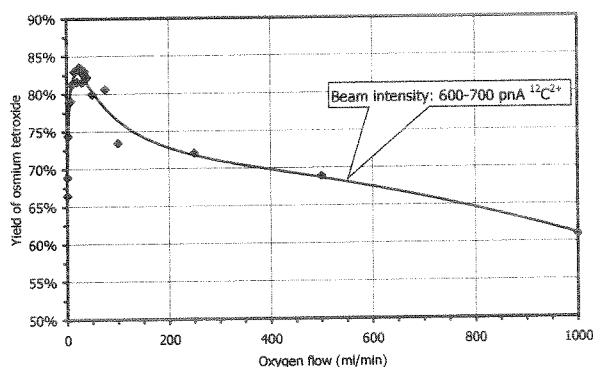

Figure 2: Dependence of the absolute yield of osmium tetroxide on the oxygen flow

The yield also depends on the helium flow. We found, that a helium flow of at least 500 ml/min is necessary to transport the volatile oxide efficiently.

Because of the clusterless transport, only volatile by-products are able to leave the target chamber. In the nuclear fusion reaction using a ^{12}C-beam, ^{18}F and ^{15}O are formed as by-products. We investigated in their removal.

The volatile oxides can be deposited directly on glass fibre filters, soaked with sodium hydroxide, which was done in the optimisation of the transport efficiency, and on metallic surfaces (Fig. 3).
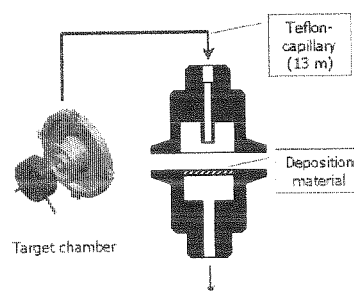
Figure 3: Basic scheme of the deposition process

RuO_4 can be deposited more easily, because it is more reactive than OsO_4. For the deposition of OsO_4, very reactive and alkaline materials, like metallic sodium, can be used efficiently (Fig. 4).
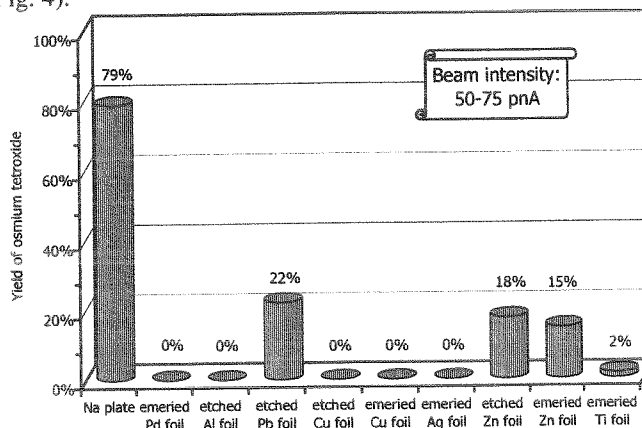
Figure 4: Comparison of different metallic surfaces for the deposition of gaseous, carrier-free OsO_4

In order to be able to perform isothermal gas chromatography at low temperatures, water vapour had to be removed from the transport gas. To this end, a drying unit, using molsieve, $Mg(ClO_4)_2$ and Sicapent®, was implemented and the concentration of water was lowered from about 300 ppm to about 6 ppm.

It should be possible to stick the volatile oxides after the isothermal gas chromatography section to clusters, so different recluster chambers were installed. These clusters are subsequently deposited on thin foils by impaction inside the rotating multidetector apparatus, ROMA, for detection.

HITGAS Efficiency in the Seaborgium Oxide Hydroxide Experiment

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The chemistry efficiency of the high temperature gas chromatography apparatus HITGAS in the seaborgium oxide hydroxide experiment is calculated with the spectra from tungsten isotopes which are produced as monitor nuclides during the seaborgium experiment.

Introduction

A first determination of the chemistry efficiency of the high temperature gas chromatography apparatus HITGAS [1] for the group 6 oxide hydroxide system was carried out in [2]. For 1350 K isothermal temperature we obtained 53 % efficiency for ^{166}W and 63 % for ^{168}W.

Unfortunately, this approach requires similar pressures in the target chamber in both experiment parts [2] because the aerosol attachment of the nuclear reaction products is pressure dependent. This could not be adjusted in our seaborgium experiment at GSI [1].

Algorithm

With the following quantities and equations we estimated the HITGAS efficiency from on-line gamma spectra.

$fh;r$	indices indicating filter holder and ROMA
$\dot{n}$	nuclide production rate
n_0	number of atoms collected during $t_{coll,r}$
λ	nuclide decay constant
$t_{coll,x}$	sample collection period; $x = fh, r$
t_{jet}	gas jet transport time
t_{step}	duration of ROMA step movement
t_{int}	ROMA step interval length; $t_{int} = t_{coll,r} + t_{step}$
$\varepsilon_{det,x}$	detection efficiency; $x = fh, r$
ε_{jet}	gas jet efficiency
ε_{hitgas}	chemistry efficiency of HITGAS
J	number of ROMA detection places
$J+1$	number of ROMA deposition places
K	actual ROMA detector place
L	number of ROMA wheel rotations during $t_{coll,r}$
N	number of ROMA deposition places which were counted N times
$J+1-N$	number of ROMA deposition places which were counted $(N-1)$ times
D_x	number of detections during $t_{coll,x}$; $x = fh, r$

In a first step, the production rate of the nuclide under study is determined with a catcher foil experiment.

In a following direct catch experiment, the gas jet is directed to a glass fiber filter holder which is counted during the nuclide collection. Eq. 1 expresses the measured number of nuclide detections. A simple rearrangement gives the gas jet efficiency.

$$D_{fh} = \dot{n} \cdot e^{-\lambda \cdot t_{jet}} \cdot \left(t_{coll,fh} - \frac{1 - e^{-\lambda \cdot t_{coll,fh}}}{\lambda} \right) \cdot \varepsilon_{det,fh} \cdot \varepsilon_{jet} \quad (1)$$

Finally, the nuclide accumulation onto the ROMA wheel is detected on-line during a HITGAS experiment. Eq. 2 describes the number of collected atoms in one ROMA deposition place during one sample collection period:

$$n_0 = \dot{n} \cdot \frac{1 - e^{-\lambda \cdot t_{coll,r}}}{\lambda} \cdot e^{-\lambda \cdot t_{jet}} \cdot \varepsilon_{jet} \cdot \varepsilon_{hitgas} \quad (2)$$

This unknown number can be calculated from the number of detections which are measured in the ROMA over a longer period (L wheel rotations) with eq. 3 and the abbreviations a, b, and c:

$$D_r = n_0 \cdot a \cdot [N \cdot b + (J + 1 - N) \cdot c] \quad (3)$$

$$a = \frac{e^{-\lambda \cdot t_{step}} \cdot e^{-(K-1) \cdot \lambda \cdot t_{int}} \cdot (1 - e^{-\lambda \cdot t_{coll,r}}) \cdot \varepsilon_{det,r}}{1 - e^{-(J+1) \cdot \lambda \cdot t_{int}}} \quad (4)$$

$$b = L - \frac{1 - e^{-L \cdot (J+1) \cdot \lambda \cdot t_{int}}}{e^{+(J+1) \cdot \lambda \cdot t_{int}} - 1} \quad (5)$$

$$c = L - 1 - \frac{1 - e^{-(L-1) \cdot (J+1) \cdot \lambda \cdot t_{int}}}{e^{+(J+1) \cdot \lambda \cdot t_{int}} - 1} \quad (6)$$

The HITGAS chemistry efficiency remains as the only unknown in eq. 2 and can be calculated easily.

Results

The results are shown in the table. The efficiency for ^{168}W agrees very well with that determined in [2]. The low efficiency for ^{166}W indicates a HITGAS dwell time between 10 and 20 seconds. This was already obtained with a yield curve Monte Carlo simulation in [2].

However, all tungsten peaks in the on-line gamma spectra of the seaborgium experiment [1] had a poor signal-to-noise ratio. Therefore, we consider our results from [2] to be more precise.

Nuclide	Half Life [s]	HITGAS Efficiency
^{166}W	18.8	30 %
^{168}W	51	60 %
^{169}W	76	40 %
^{171B}W	642	50 %

Acknowledgments

References

[1] S. Hübener, et. al., PSI Annual Report 1998, Annex IIIA, 9

[2] A. Vahle, et. al., Radiochimica Acta **84**, 43 (1999)

ANION-EXCHANGE BEHAVIOR OF TUNGSTEN AND MOLYBDENUM AS HOMOLOGS OF SEABORGIUM (ELEMENT 106) IN HNO3/ HF-SOLUTIONS

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The first aqueous chemistry of Seaborgium (element 106, Sg) showed that it forms neutral or anionic oxyfluorides in 0.1 M $HNO_3/5*10^{-4}$ M HF [1], but the experiment did not determine a distribution coefficient. In our future experiments with ^{265}Sg, we plan to determine K_d-values on an anion exchanger in HF/ 0.1 M HNO_3 and pure HCl solutions using on-line chromatography with the multi-column technique [2]. In preparation of this experiment, we have measured the K_d-values of short-lived Hf [3] and W [4] using the multi-column technique and compared these with results obtained with ARCA.

Recently, prior to the studies with Seaborgium, we have investigated the chemical behavior of its homologs tungsten and molybdenum on cation and anion exchangers in HF/HNO_3 and pure HNO_3 and HCl solutions in batch experiments as well as with ARCA. We report here the results obtained from batch experiments with neutron activated ^{187}W and carrier free ^{99}Mo. These data are compared with those obtained with ARCA, involving 76-s ^{165}Hf and 2.4-min ^{170}W produced on-line by the reactions ^{158}Dy(^{12}C, 5n) and ^{nat}Er(^{12}C, xn), respectively, at the UNILAC at GSI.

Figure 1 shows the results from the batch experiments with ^{187}W and ^{99}Mo using varying concentrations of HF in 0.1 M HNO_3 (HCl). The situation is complex due to a competition between hydrolysis and fluoride complexation. In the case of tungsten, the minimum in the K_d-values at 0.01 M HF indicates that, for lower HF concentrations, high K_d-values due to the presense of anionic hydrolysis products are decreased with increasing HF concentration as a result of increasing charge neutralization by the addition of fluoride ligands. The increase of the K_d-values for >0.01 M HF is obviously due to the formation of anionic fluoride complexes. For Mo, the dependence of the K_d-values on HF concentration is less structured.

Figure 2 compares the K_d-values for Mo and W at 0.005 M HF as a function of the concentration of the counter ion NO_3^- which competes for the binding site on the anion exchanger. The lower slope for W is consistent with the presence of some neutral species along with anionic ones. At 0.1 M HF, slopes similar to that for Mo in Fig. 2 are observed for both Mo and W. The latter HF concentration is too high for a seaborgium experiment with the multi-column technique as the decay product Rf forms neutral or anionic fluoride complexes under these conditions which break through a cation-exchange filter [5].

Fig. 3 shows the K_d-values of Mo and W in the absence of HF in both HNO_3 and HCl. At low mineral acid concentrations, the sequence of the K_d-values, Mo>W, reflects the known fact that Mo is more hydrolysed than W [6]. The decrease of the K_d-values for >0.01 M HNO3 or HCl is due to the action of the counter ions NO_3^- and Cl^- where NO_3^- competes more effectively for the binding sites than Cl^-. By calculating the electronic structure and by applying her theoretical treatment of hydrolysis, V. Pershina predicts the sequence Mo>W>Sg in dilute mineral acids.
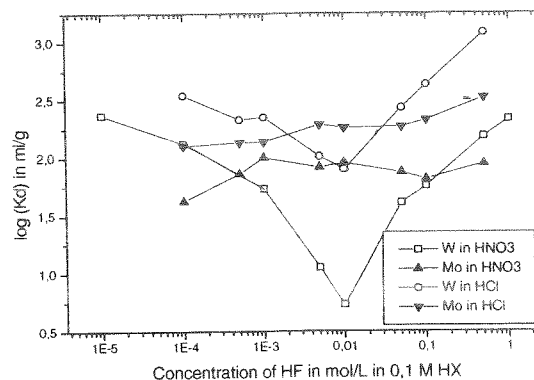

Fig. 1 K_d-values of W and Mo at variable HF-concentration and 0.1 mol/l HNO_3 or HCl on Dowex 1X8
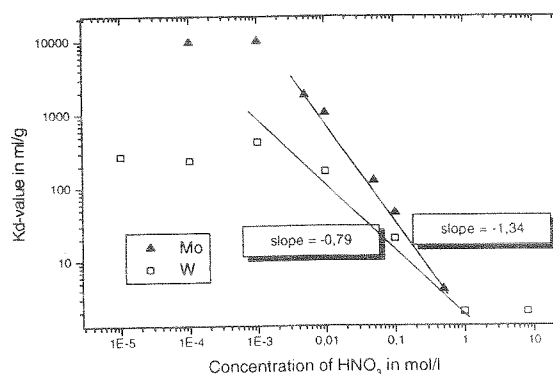

Fig. 2: Dependence of the K_d-values of Mo /W on varying HNO_3-concentration at 0.005 M HF on DOWEX 1X8
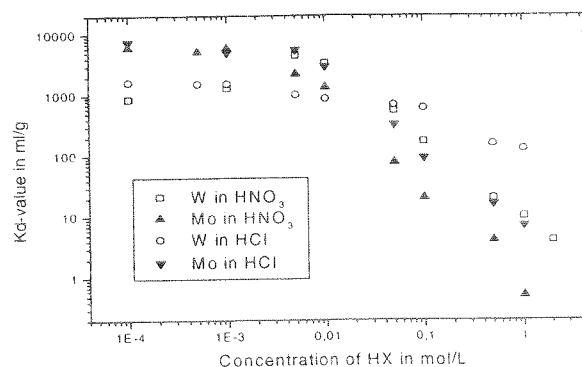

Fig. 3: Dependence of the K_d-values of Mo /W on varying HNO_3 / HCl concentration on DOWEX 1X86

References

[1] M. Schädel et al., Radiochim. Acta 77, 149 (1997)

[2] G. Pfrepper et al., Radiochim. Acta 77, 201 (1997)

[3] A. Kronenberg et al., GSI annual report 1998, p. 171

[4] A. Kronenberg et al., PSI annual report 1998, p. 7

[5] E. Strub et al., GSI Annual Report 1998, p. 15

[6] Baes, Mesmer, Hydrolysis of Cations; Wiley, 1976

FROM ARCA TO KRAUT: ON THE HOMESTRETCH FOR A SEABORGIUM REDUCTION EXPERIMENT

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Tungsten (W) and Molybdenum (Mo) as homologs of seaborgium (Sg) are used to develop a reduction experiment for Sg. Previous studies [1,2,3] with carrier free amounts of W or on-line produced W had shown that it is possible to reduce W(VI) to W(III) in a heterogenic system with Aluminium as reducing agent at a solution temperature of about 80°C.

A modified version of the Automated HPLC Apparatus ARCA II [4] was used to separate unreduced from reduced W. While W(VI) sticks to an anion exchange (AIX) column in 0.1 M HCl/0.1 M HF, W(III) does not form anionic complexes and runs through the column.

W produced on-line at the GSI UNILAC in the reaction $^{nat}Er(^{12}C,xn)^{170,171,172...}W$ was transported to ARCA II with a He/KCl gas jet system. After a collection time of 120 s, the KCl spot was dissolved in 333 μl of a solution of 0.1 M HCl/0.1 M HF. The solution passed a heated "reduction column" filled with Al wire and was fed onto an AIX column at a flow rate of 1ml/min. As described above, W(III) runs through this column and is collected in the elution fraction. W(VI) sticks to the column. The W in the elution fraction was detected by γ-spectroscopy.

Reference values were taken

a) directly from the cluster jet (100% value)
b) through the empty system (without Al, without AIX) to verify the 100% value
c) through the system without AIX ("elution yield")
d) through the system without Al to demonstrate that W(VI) is not eluted from the column.

The temperature of the reduction column was varied. Because the used thermo couple could not be placed directly at the reduction column, a temperature calibration was measured correlating the thermo couple (outer) temperature with the solution (inner) temperature.

The results of the reduction experiments are shown in Fig.1: At room temperature, W is not reduced and is adsorbed on the AIX, while at higher temperature, about 55% of the activity can be eluted. It should be noticed that these 55% are an overall chemical yield (left scale) including losses due to both incomplete reduction and incomplete elution.

If the data are recalibrated for losses in the reduction unit (determined by the reference value c) and the temperature measurement, the on-line data are in full agreement with the offline data (see [3]).

The size of the reduction column was optimized such that i) the influence of the Al losses due to dissolution in the eluent is minimal and ii) the reduction yield is maximal (about 80% as reached in off-line experiments before).

The results from the experiments with ARCA II led to the development of a special apparatus that will be used in a forthcoming Sg reduction experiment, KRAUT ("Kreisförmige Reduktions-ARCA zur Unterstützung bei Transactinidenexperimenten"; circular reduction ARCA for transactinide experiment assistance).

In KRAUT, the reduction unit is separated from the collection unit and the separation unit to prevent deformations due to heat. The columns used in KRAUT are recycled while the apparatus is running. Thus, the collection time can be reduced in a Sg experiment resulting in higher gas jet yields $(T_{1/2}(^{265}Sg)=7.4$ s [5]). The number of movable parts of KRAUT was reduced to a minimum. This allows a reliable operation during the extended times that are needed to examine and detect nuclear reaction products with cross sections in the sub-nb range.

First tests of KRAUT with Mo from thermal neutron fission of ^{235}U have been performed at the TRIGA reactor in Mainz.
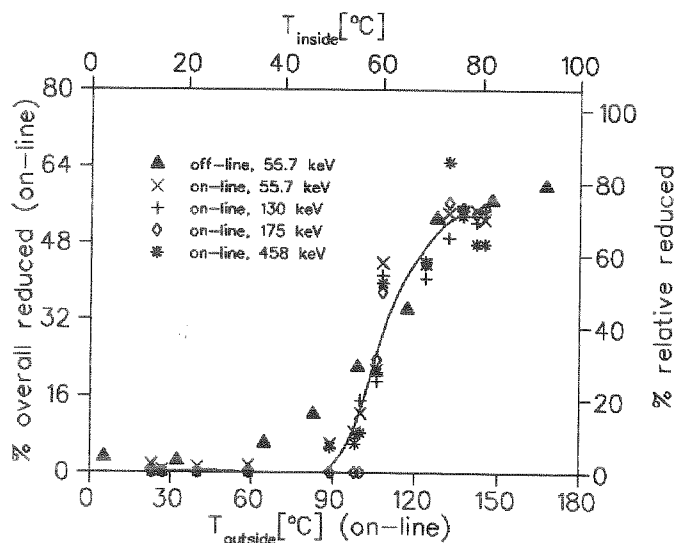

Fig.1: Temperature dependence of the reduction of W(VI) with Al. Reduced and unreduced species are separated by an anion exchange column (Dowex AG1x8). The on-line data (open symbols and fitted line) are in good agreement with the off-line data (solid triangles).

REFERENCES

[1] E. Strub, Diplomarbeit, Universität Mainz, 1997
[2] E. Strub et al., GSI Scientific Report 1997, 208
[3] E. Strub et al., GSI Scientific Report 1998, 195
[4] M. Schädel et al., Radiochim. Acta 48, 171 (1989)
[5] A. Türler et al., Phys. Rev. C, 57, 1648 (1998)