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GAS PHASE CHEMISTRY OF SUPERHEAVY ELEMENTS

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Abstract

In recent years chemistry of heaviest elements has gained considerable interest. The discovery of isotopes with sufficiently long half lives now make chemical investigations of elements with atomic numbers up to Z=118 feasible. The challenge of such investigations is to search for relativistic effects, predicted to increasingly influence chemical properties. However, experimental conditions are extremely difficult due to the fact, that heaviest elements can only be produced at large accelerator facilities and at a one-atom-at-a-time level. Moreover, formed isotopes are usually short-lived, with half-lives of a few seconds.

This overview summarizes gas chemical studies of transactinides using two approaches, gas thermochromatography and isothermal gas chromatography. Both techniques enabled successful first chemical studies of transactinides, i.e. of rutherfordium (Z=104, Rf), dubnium (Z=105, Db), seaborgium (Z=106, Sg), bohrium (Z=107, Bh), hassium (Z=108; Hs) and the yet unnamed elements 112 and 114, respectively. Typically, these chemical investigations were performed with less than 20 atoms.

The elements Rf through Hs showed a typical behaviour of a d-element, resembling much the expected trend within their respective group of the periodic table. This also holds for element 112 with a filled 6d and 7s shell. In most recent experiments evidence was found for an unexpected behaviour of element 114, being more noble gas like rather than resembling the behaviour of a typical group 14 member.

1. Introduction

In transactinide chemistry research, gas phase separation procedures play an important role. Already, the very first investigation of rutherfordium has been conducted in form of frontal isothermal gas chromatography in a chlorinating atmosphere [1]. Several reasons are responsible for this success: gas phase reactions are fast and can be easily adapted to accelerators (gas-jet technique). In addition, after chemical separation, very thin final samples can be prepared which is mandatory for detection of α-particles with high energy resolution. This enables identification of heavy element isotopes which decay predominantly via α-emission.

2. Rutherfordium (Rf Element 104)

So far, most gas chemical investigations of this element have been conducted in form of its chloride, oxochloride or bromide. Only in one experiment an attempt was made to search for a p-element behavior of Rf, based on a predicted ground state configuration of $[Rn]5f^{14}7s^{2}7p^{2}$ [2] or, from a more recent calculation $[Rn]5f^{14}6d7s^{2}7p$ [3], rather than the expected “d-like” $[Rn]5f^{14}6d^{2}7s^{2}$. However, the experiment yielded no evidence for a “Pb-like” behavior of Rf [4]. This observation is not surprising, since Multi-Configuration Dirac-Fock (MCDF) calculations showed that ionization potentials, atomic and ionic radii for Rf are very similar to those of Hf [3].

2.1 VOLATILE COMPOUNDS OF RUTHERFORDIUM

Due to the high sublimation enthalpies of group 4 elements, gas chromatographic separations of the atoms are not feasible in quartz columns. Under halogenating conditions, however, group 4 elements form mono-molecular pure halides such as tetra fluorides, chlorides, bromides and iodides.

A good measure of the volatility is the vapor pressure. Figure 1 depicts the vapor pressure curves for Zr and Hf halides in the gas phase over the respective solids. As can be seen, the volatility decreases according to MCl_4 > MBr_4 > MI_4 > MF_4 with M= Zr and Hf. Evidently, chlorides and bromides are clearly the best choices for gas chemical studies. Iodides have the disadvantage of a poor thermal stability and fluorides are least volatile.

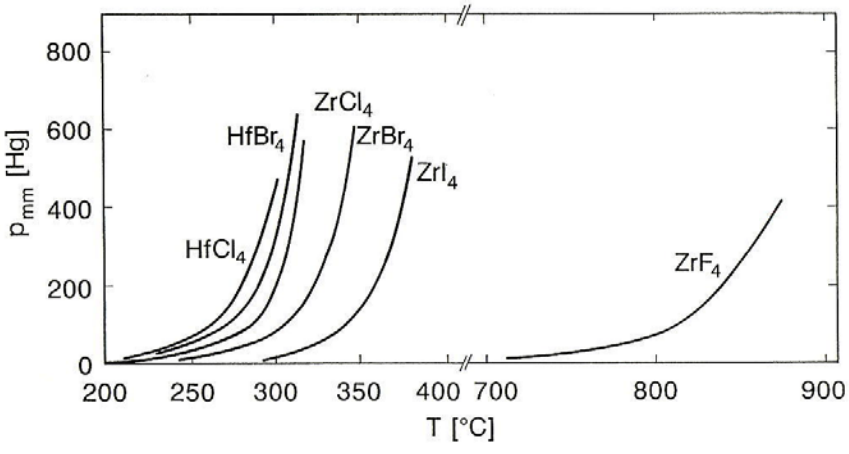

Fig.1. Vapor pressure curves for Zr and Hf halides over their respective solids. Reproduced from [5].

In principle, in oxygen containing carrier gases also oxohalides can be synthesized. However, for group 4 elements little is know about these compounds. It was observed that $ZrOCl_2$ and $HfOCl_2$ decompose to tetrachlorides and the oxide under elevated temperatures [6]. An alternative process is substitutive adsorption of the pure halides on the surface of the quartz chromatography column where oxochloride formation is possible in the adsorbed state only.

2.2 EARLY GAS CHEMICAL STUDIES WITH RUTHERFORDIUM

The first chemical study of Rf [1] was part of the discovery claim of this element by the Dubna scientists. For production of the isotopes ^{259,260}Rf the hot fusion reaction ^{22}Ne + ^{242}Pu was used. In these pioneering studies isothermal frontal gas chromatography experiments showed that in a chlorinating gas Rf forms a highly volatile molecule. As chlorinating agent 0.15 mm Hg vapour pressure of $NbCl_5$ / $ZrCl_4$ was added to a flowing N_2 carrier gas. The gas then passed through an isothermal glass column kept at temperatures between 250 and 300 °C. From previous experiments it was known that actinides do not form sufficently volatile chlorides that could pass the column at such moderate temperatures.

Behind the column mica solid state detectors were positioned. They were kept at lower temperatures in order to adsorb the $RfCl_4$ molecules. It was assumed that the produced isotopes of Rf decay at least partly by spontaneous fission. Mica is known to be well suited for identification of latent fission tracks. In a series of experiments that accumulated a total beam dose of $4x10^{18}$ beam particles 65 fission tracks were detected along the mica detectors. These fission events were assigned to a spontaneously-fissioning isotope of Rf, presumably ^{260}Rf. Later, this assignment was questioned since additional measurements proved that this isotope has a half-life of only 20 ms, too short for chemical study. It was therefore concluded that ^{259}Rf with a half-life of 3 s and an assumed small fission branch was the isotope that labelled the separated molecule.

After these very first experiments the Dubna group applied the thermochromatography technique that permits to compare the volatility of the Rf species, measured via the deposition temparature in the chromatographic tube, with those of the Hf compounds. An example of such a study is depicted in Figure 2. From the observed very similar deposition temperature of the Rf and Hf chlorides it was concluded that both elements behave very similarly, therefore convincingly proving that Rf is a d-element [7]. Recently, the chromatographic peaks shown in Figure 2 have been analysed applying a Monte-Carlo model. Based on some assumptions on the adsorption process and assuming that indeed the decay of ^{259}Rf with a half-life of 3 s has been detected, the standard enthalpies of adsorption, ΔH_a^0, of -110 kJ/mol and –146 kJ/mol for Rf and Hf on the quartz chromatography column surface were deduced [8].

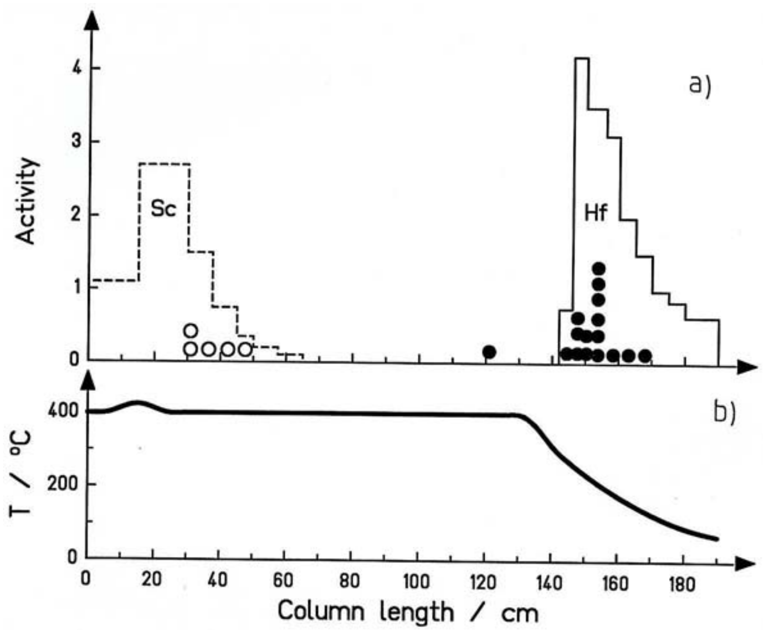

Fig.2. Results of an experiment to investigate the volatility of ^{259}Rf – and ^{170,171}Hf chlorides, a) temperature profile in the column, b) distribution of fission tracks (open and closed circles), ^{44m}Sc (a representative of a actinides-like element), and of ^{170,171}Hf. Reproduced from [7].

Thermochromatography was also applied to investigate the volatility of Rf and Hf bromides [9]. These experiments yielded evidence that Rf bromide is more volatile than Hf bromide, but also more volatile than Rf chloride. This observation is in contradiction to later studies (see below).

2.3 ON-LINE ISOTHERMAL GAS CHEMICAL INVESTIGATIONS OF RUTHERFORDIUM

2.3.1 *General remarks*

In recent years predominantly continuous isothermal chromatography has been applied in gas chemical studies of transactinides. This technique offers the possibility to combine a continuous separation of volatile species with an *in-situ* detection of the products on the basis of single atom counting. To reach this ambitious goal, novel devices have been developed such as OLGA (On-Line Gas chemistry Apparatus) [10] or, in a modified version, HEVI (Heavy Element Volatility Instrument) [11].

On-line isothermal gas chemistry has originally been developed to search for superheavy elements with atomic numbers between 112 and 118. OLGA I was restricted to an operation with inert gases. Its application concentrated on separations of volatile atoms. As “reactive” gas, traces of hydrogen gas could be added to a helium carrier gas in order to stabilize the elemental state. Model studies with the p-elements Po, Pb, Bi and At showed that at temperatures of up to 1000 °C excellent separations of these elements from d- and f-elements could be achieved.

Improved versions of OLGA (versions II and III) enabled the applications of corrosive gases such as hydrogen chloride or hydrogen bromide, chlorine, thionyl chloride or boron tribromide vapor etc. This made it possible to synthesize volatile halides and measure their retention times in isothermal quartz columns.

2.3.2 *Isothermal gas chromatography studies of $RfCl_4$ and $RfBr_4$*

For investigations of the chlorides and bromides commonly the isotope ^{261}Rf was used as tracer. It has a half-life of 78 s and can be produced in the fusion reaction $^{18}O + ^{248}Cm$ at a bombarding energy of about 100 MeV. ^{261}Rf decays via emission of two sequential α-particles via ^{257}No to ^{253}Fm, a long-lived product. Hence, identification of ^{261}Rf after chemical separation bases on the measurement of the two life times and two α-decay energies of the mother and its daughter nuclide, respectively. From the four signals an unequivocal identification of every decaying atom of rutherfordium may be achieved. Simultaneous formation of Hf isotopes may be obtained by covering the ^{248}Cm target by a thin layer of Gd.

Figure 3 depicts the result from such a study with the OLGA III device [12]. Helium saturated with carbon particles served as carrier aerosol to transport the products from the collection chamber to the chemistry device. The chemical reagent was HCl gas, purified from traces of oxygen, added to the carrier gas at the entrance of the oven system.

Rf passes through the quartz column at a lower retention temperature compared to Hf. This observation received considerable attention and was interpreted as evidence for relativistic effects, since the higher volatility of $RfCl_4$ compared to that of $HfCl_4$ is unexpected on the basis of classical extrapolations.

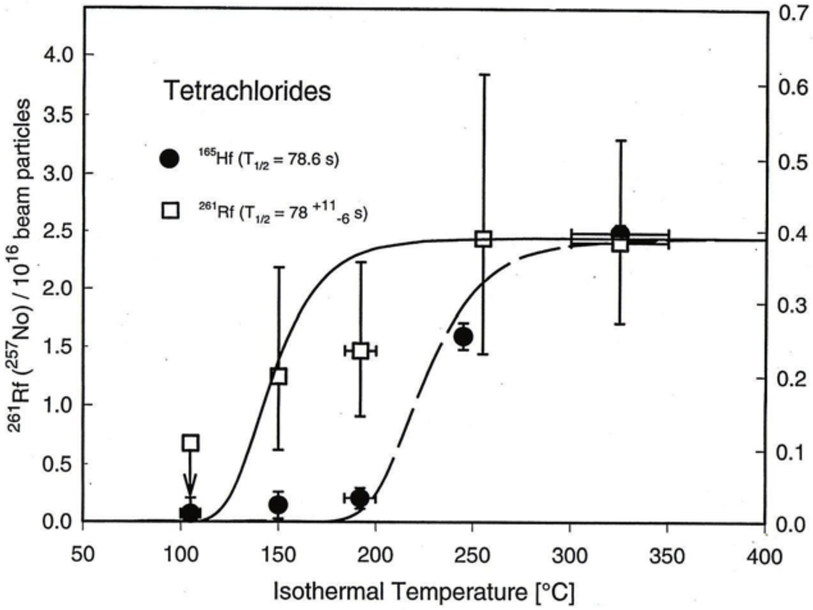

Fig.3. Relative yields for $^{261}RfCl_4$ and $^{165}HfCl_4$ from in the same $^{18}O + ^{248}Cm/^{152}Gd$ experiment behind the isothermal quartz chromatography column as a function of the temperature. The solid lines represent Monte Carlo simulations adapted to the experimental data. Reproduced from [12].

In an earlier study with the device HEVI the chlorides of Zr, Hf, and Rf were investigated employing the reactive gases HCl/CCl_4 (Zr, Hf) and HCl (Rf). MoO_3 particles in a He carrier gas served as aerosol [13]. In contact with HCl, MoO_3 forms a very volatile molybdenum oxochloride that passes through the chromatographic column without deposition on its surface. For Rf and Hf chlorides the same sequence in volatility was found as depicted in Figure 3. In addition, the volatility of Zr chloride turned out to be very similar to that of Rf chloride, hence, different to the volatility of Hf chloride. This observation is rather unexpected, since the volatilities of macro amounts of Zr and Hf tetrachlorides are nearly identical (Figure 1).

A first study of Rf bromide with OLGA II indicated that Rf is more volatile than Hf bromide [14]. For the transport KCl was used as aerosol particles and HBr/BBr_3 served as reactive gas. In addition, Rf bromide was found to be less volatile compared to the Rf chloride. In a more recent study with HEVI, using KBr particles and HBr as brominating agent, these findings were essentially confirmed (Figure 4). The behavior of Zr and Hf bromides were found to be very similar being less volatile than Rf bromide [15].

2.3.3 *Oxochlorides of Rf*

The oxochlorides of group 4 elements are expected to be less stable than the pure chlorides. $ZrOCl_2$ and $HfOCl_2$ were found to decompose to the tetrachlorides at elevated temperatures [6]. It is therefore not clear, whether $ZrOCl_2$ and $HfOCl_2$ exist in the gas phase.

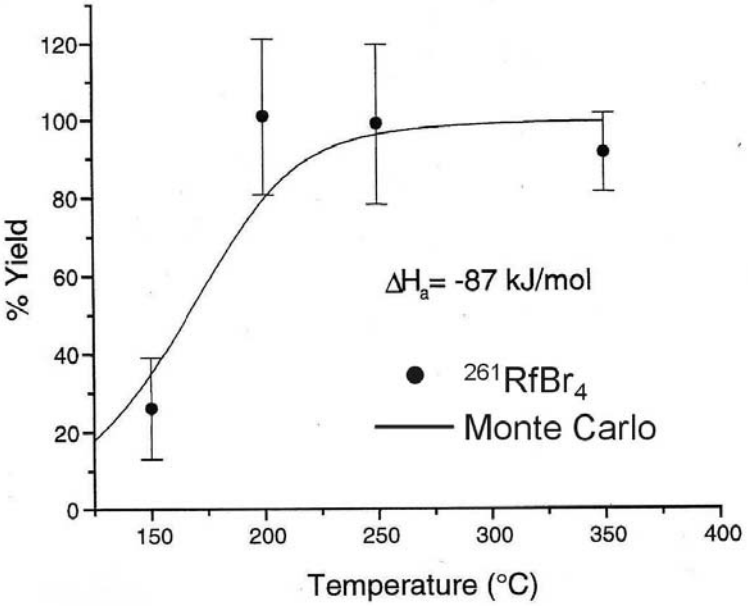

Fig.4. Chromatographic yield curve for ^{261}Rf bromide using KBr aerosol particles for transport and HBr as reactive gas. Reproduced from [15].

In thermochromatography experiments an increase of the deposition temperature of Zr and Hf was observed as a function of the partial pressure of oxygen in a chlorinating reactive gas mixture [16]. An OLGA III study with oxygen containing chlorinating reactive gas confirmed this observation: Rf and Hf were considerably less volatile compared to oxygen-free conditions (Figure 5).

It was speculated that the oxochlorides do not exist in the gas phase but only in the adsorbed state. The following transport mechanism was proposed:

$$MCl_{4(g)} + \frac{1}{2} O_2 \Leftrightarrow MOCl_{2(ads)} + Cl_{2\,(g)}$$

It is interesting to note that $RfOCl_2$ and $HfOCl_2$ behave much more similar compared to the pure chlorides $RfCl_4$ and $HfCl_4$.

2.3.4 *Adsorption enthalpies of Zr, Hf, and Rf chlorides and bromides on quartz*

From the measured chromatographic retention temperatures adsorption enthalpies ΔH_a^0 of single molecules on the surface of the quartz chromatography column can be deduced. This analysis is based on certain thermodynamic assumptions of the adsorption process of single molecules with the surface of the chromatographic column [18]. In addition, a Monte Carlo model enables to describe the migration path of each single molecule along the chromatographic column under real experimental conditions [19].

Figure 6 summarizes resulting ΔH_a^0 values from isothermal gas chromatographic investigations of the pure chlorides and bromides of Zr, Hf, and Rf, respectively, using the HEVI and OLGA II devices [20]. A smooth (classical) extrapolation of the ΔH_a^0 values from Zr through Hf shows that one would expect the ΔH_a^0 values for $RfCl_4$ or $RfBr_4$ to be more negative than those of the respective Hf compounds. The experimental values for Rf show a striking reversal of this expected trend. In addition, the bromides have more negative values, hence being less volatile than the corresponding chlorides.

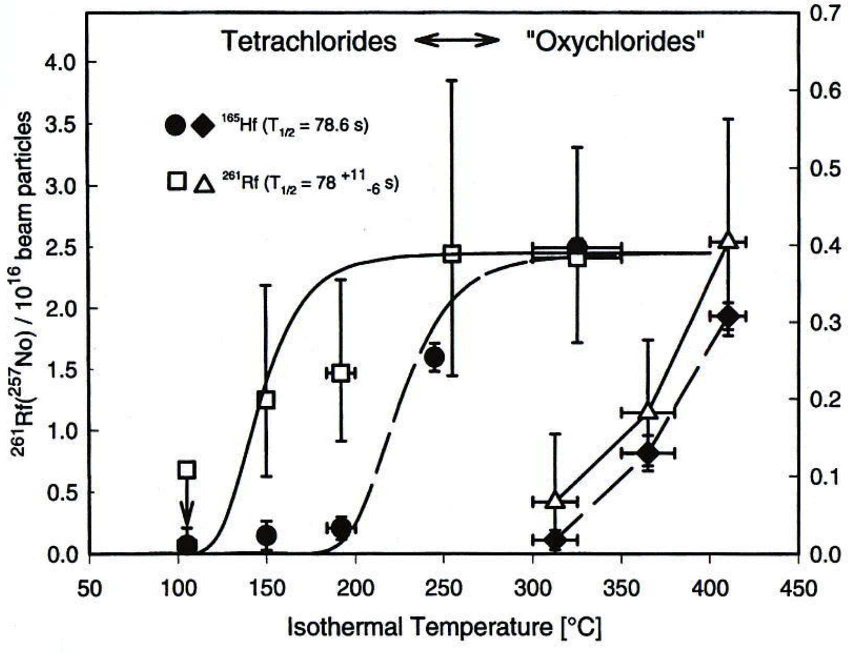

Fig.5. Yields for ^{261}Rf and ^{165}Hf with Cl_2, saturated with $SOCl_2$ vapor and with O_2 in comparison with the pure halides. Reproduced from [17].

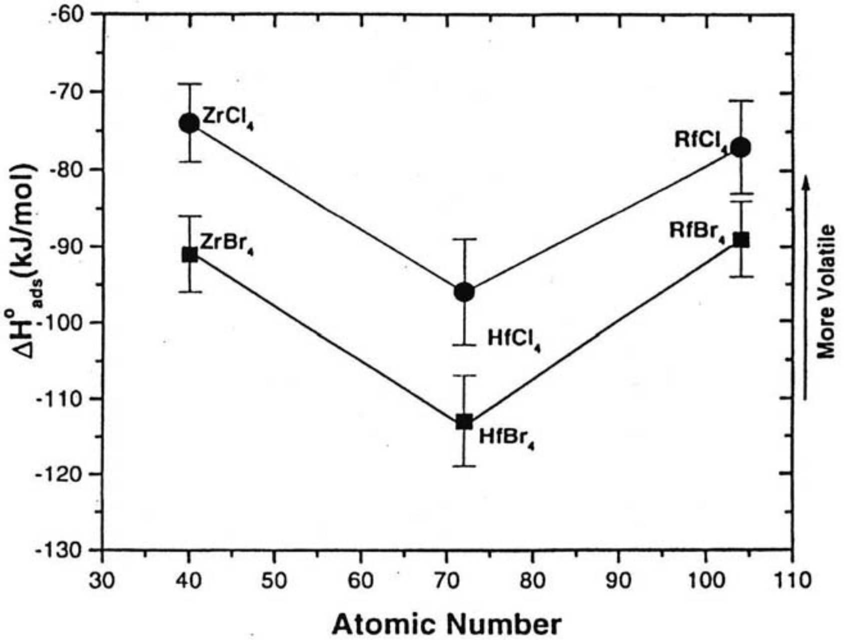

Fig.6. Adsorption enthalpies of chlorides and bromides of Zr, Hf, and Rf on quartz surfaces, deduced from OLGA and HEVI experiments. Reproduced from [20].

Relativistic calculations of the chemical properties of these compounds predict trends that are in agreement with experimental observations. Therefore, it was argued that this “reversal” in the trend of ΔH_a^0 for chlorides and bromides when going from Zr via Hf to Rf is evidence for “relativistic effects” in the chemistry of Rf [17].

3. Dubnium (Db, Element 105)

Dubnium is expected to have a $[Rn]5f^{14}6d^{3}7s^{2}$ electronic ground state configuration, being a firm member of group 5 below tantalum.

All gas chemical investigations of dubnium have been performed with Db^{5+} in form of the penta halides (chlorides and bromides) and oxohalides. All these studies were extremely difficult due to the high tendency of group 5 elements to react with trace amounts of oxygen or water vapor. Hence, gas chemical investigations were only successful if the quartz chromatography columns were very carefully preconditioned with the halogenating reactive gas prior to each experiment and, in addition, applying extensive cleaning procedures to the carrier gas to remove trace amounts of oxygen and water vapor.

3.1 VOLATILE COMPOUNDS OF DUBNIUM

Group 5 elements are most stable in their maximum oxidation state +5 and therefore form pentahalides (Figure 7). Most volatile are the pentafluorides, followed by the pentachlorides and the pentabromides. Besides the pure halides, also the oxohalides (MOX_3) are stable in the gas phase. They are less volatile compared to the pure halides. This was confirmed experimentally for niobium (Figure 8).

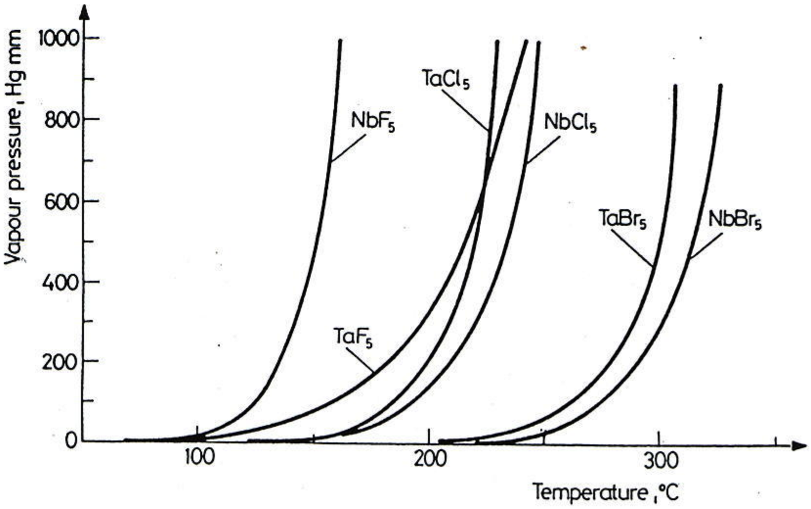

Fig.7. Vapor pressure curves for Nb and Ta halides over the respective solids. Reproduced from [5].

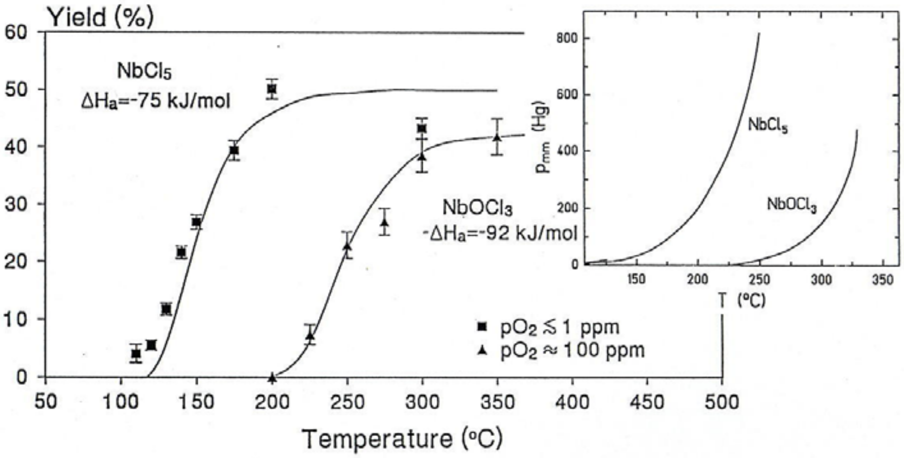

Fig. 8. Vapor pressure curves for $NbCl_5$ and $NbOCl_3$ (upper right corner) and the relative yields of $^{99g}NbCl_5$ and $^{99g}NbOCl_3$ molecules passing through an isothermal quartz column. Reproduced from [5].

3.2 EARLY GAS CHEMICAL STUDIES WITH DUBNIUM

As early as 1970 gas chemical experiments with Db have been performed in a chlorinating atmosphere [21]. These studies applied the gas thermochromatography technique and indicated that the deposition temperature of Db chloride (or oxochloride) is rather similar to that of Hf under identical conditions and significantly higher compared to the deposition temperature of Nb. Later studies were conducted in a brominating gas medium and again yielded evidence that Db bromide is less volatile compared to the homologous compound with Nb [22] (Figure 9). These investigations were performed with ^{261}Db ($T_{1/2}$ = 1.8 s) which has a small fission branch. This nuclide was produced in the ^{22}Ne + ^{243}Am reaction.

From the result of this experiment it was concluded that the boiling point of $DbBr_5$ may exceed the boiling point of $NbBr_5$ by 80-100 °C and may be close to the boiling point of $PaBr_5$. The ionic radius of Db^{5+} was estimated to be close to the radius of Pa^{5+}, which is ≈ 0.9 Å, whereas the radii of Nb^{5+} and Ta^{5+} are both ≈ 0.7 Å.

3.3 ON-LINE ISOTHERMAL GAS CHEMICAL INVESTIGATIONS OF DUBNIUM

3.3.1 *Production of dubnium isotopes*

On-line gas chemical studies of dubnium have been mostly performed with ^{262}Db. This nuclide can be produced in the reaction ^{249}Bk (^{18}O,5n) at a beam energy of about 100 MeV. It has a half-life of 34±5 s and decays with 67 % by emission of two sequential α particles via ^{258}Lr ($T_{1/2}$=4.4 s) to the long-lived ^{254}Md ($T_{1/2}$ =28m). With 33 % ^{262}Db decays by spontaneous fission. Hence, identification of each separated labeled molecule based on either detection of two α-particles and two life times or on the detection of spontaneous fission decay events including the life times of each decaying atom.

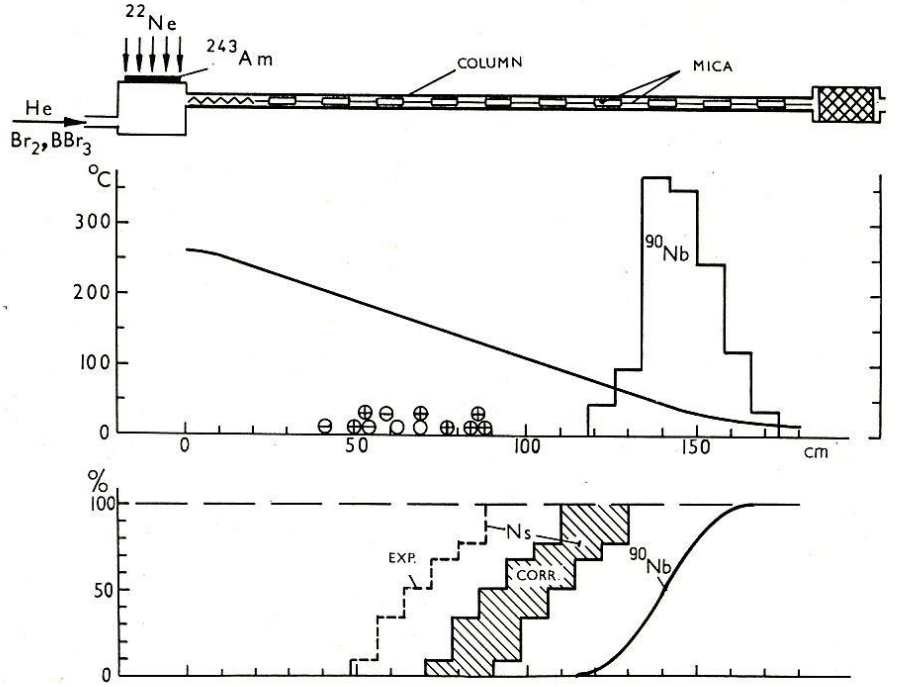

Fig.9.
Top: Schematic of the thermochromatography experiment with Db in a brominating atmosphere (Br_2+BBr_3.
Middle: Temperature profile along the column and measured distributions of ^{90}Nb and ^{261}Db.
Bottom: Integral distribution of ^{90}Nb (solid line) and of Db (named Ns by the authors at that time; shaded area) after corrections for the much shorter half-life of ^{261}Db compared to that of ^{90}Nb. Reproduced from [22].

3.3.2 *Chlorides and oxochlorides*

Several attempts to form in on-line isothermal gas chromatographic investigations with the OLGA system the pure pentachloride of Db failed. Obviously, despite very thorough cleaning procedures, minute amounts of oxygen and/or water vapor in the system were still sufficient to form at least partly dubnium oxochloride, most likely $DbOCl_3$. Figure 10 depicts a measured chromatographic curve in conjunction with the data for Nb from Fig. 8 [23]. As chlorinating agent HCl gas was used, purified with activated charcoal at 900 °C. The shape of the yield curves suggests two components, a species with a lower volatility passing through the column above 350 °C and one with a higher volatility that is retained in the column at 200 °C. The two species are tentatively assigned to $DbOCl_3$ and $DbCl_5$, respectively. From this follows, that $DbCl_5$ must be equal or more volatile than $RfCl_4$ (see Figure 3).

It is interesting to note that none of the gas chemical investigations succeeded to investigate the behavior of tantalum chloride. Obviously, the tendency to react with oxygen is higher for Ta compared to Nb and Db.

3.3.3 *Bromides and oxobromides*

The volatility of Dubnium bromide was studies with HBr as reactive gas using the isotope ^{262}Db formed in the ^{249}Bk (^{18}O,5n) reaction [24]. In this experiment the retention behaviors of niobium and tantalum bromides were investigated as well. Interestingly, the volatile tantalum bromide was formed only when HBr was saturated with BBr_3 vapor. The data are shown in Figure 11. A trend in volatility of Nb≈Ta>Db was deduced. This sequence is very surprising since $DbBr_5$ is expected to be more volatile compared to $NbBr_5$ and $TaBr_5$, respectively. Evidence for a lower volatility of dubnium bromide relative to that of niobium bromide has already been found in previous thermochromatographic studies (see Figure 9).

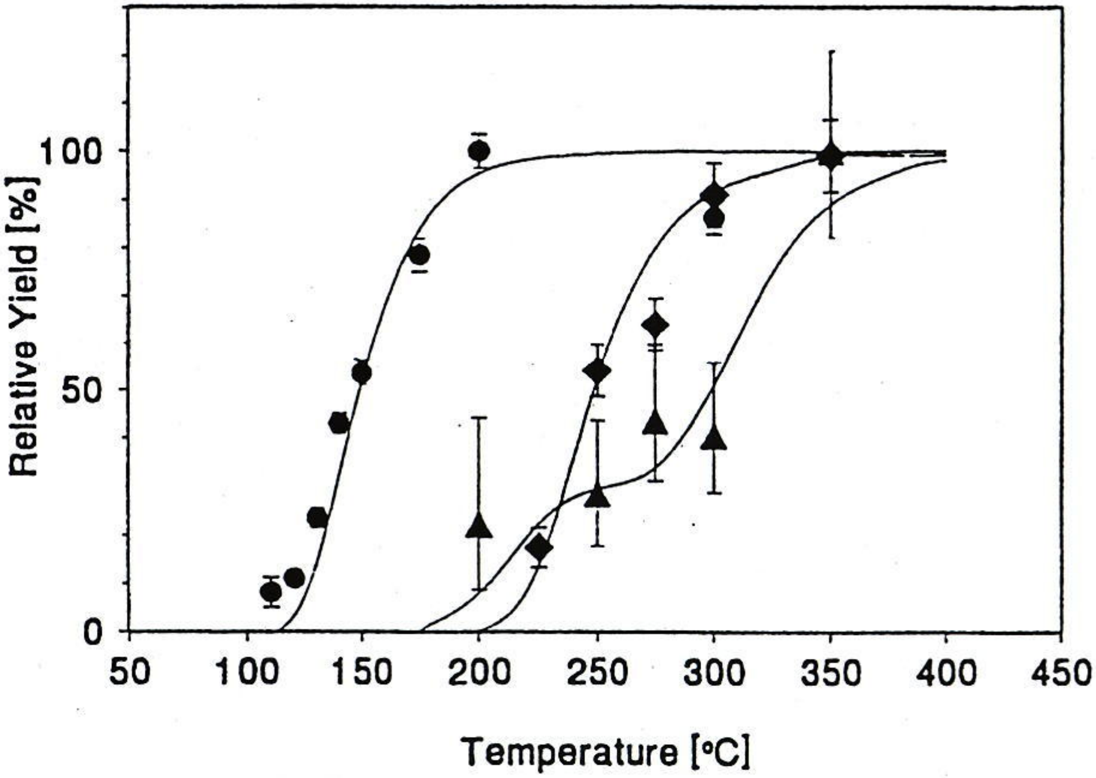

Fig.10. Relative yield of Db measured in an isothermal gas chromatographic experiment with purified HCl as reactive gas. Reproduced from [23]. For comparison, the data for Nb measured under identical gas chemical conditions from Figure 8 are also shown.

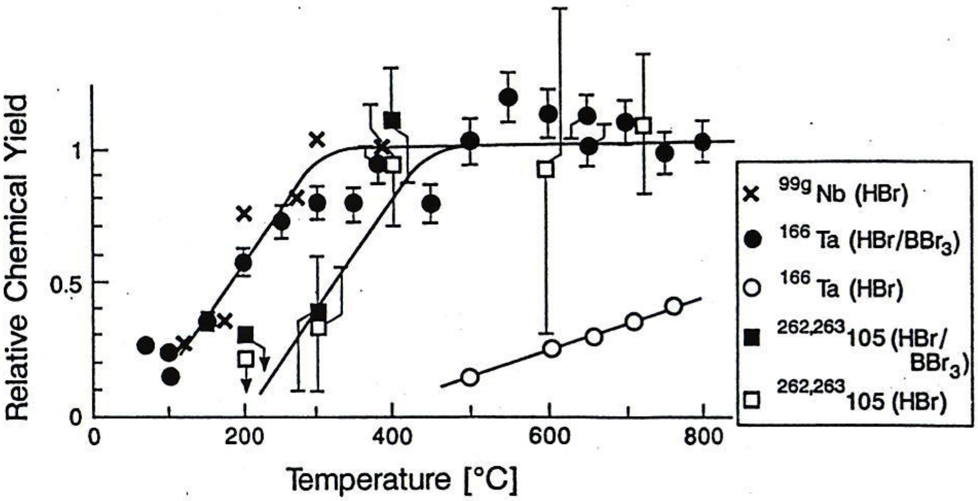

Fig.11. Yields of Nb, Ta and Db in a gas chromatographic experiment with HBr (Nb, Db) and HBr/BBr$_3$ (Db, Ta) as reactive gas. Reproduced from [24].

3.3.4 *Adsorption enthalpies of Nb, Ta and Db chlorides, oxochlorides, bromides and oxobromides on quartz*

Figure 12 depicts ΔH_a^0 values of group 5 chlorides and bromides measured with the OLGA technique (for an overview of all experimental investigations including a re-analysis of the data, see [25]). It is rather surprising to observe a different trend of the ΔH_a^0 values when going from Nb via Ta to Db, if compared to the situation in group 4 (see Figure 6). It was speculated [25], that e.g. in case of the bromides [24] the oxobromide of dubnium has been formed rather than the pure pentabromide. However, this would mean that under identical gas chemical conditions Nb and Ta form pure bromides while Db does not. If true, Db has a much higher tendency to react with oxygen compared to the lighter homologues Nb and Ta. So, presently it remains open whether the ΔH_a^0 values for Db shown in Figure 12 represent the behavior of the pure halides or at least partly of the oxohalides.

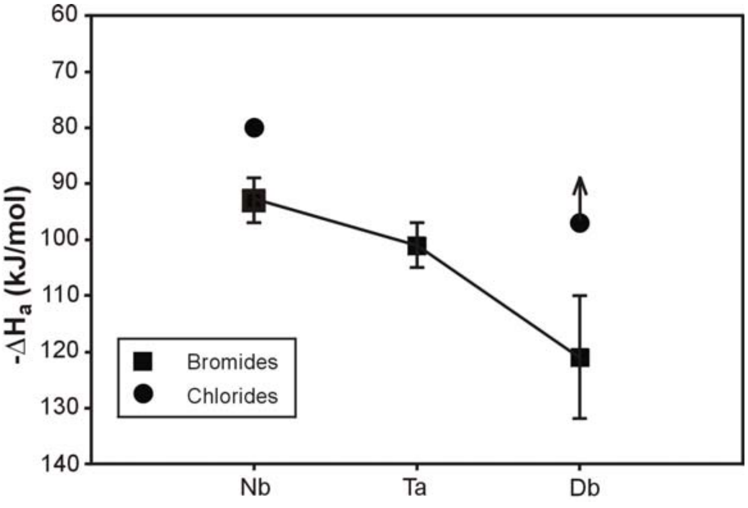

Fig.12. Adsorption enthalpies of chlorides and bromides of Nb, Ta and Db on quartz surfaces, deduced from OLGA experiments. Reproduced from [25].

4. Seaborgium (Sg, Element 106)

For over 20 years, ^{263}Sg with a half-life of 0.9 s was the longest-lived known Sg isotope. In 1992 Timokhin et al. from Dubna studied the chemical identification of Sg as volatile oxochloride making use of on-line thermochromatography [26]. This claim was substantiated by ancillary experiments [27, 28] and further studies of the behavior of homologue elements Mo and W [29]. Shortly thereafter, an international collaboration of chemists conducted on-line isothermal chromatography experiments with Sg oxochlorides [30]. The presence of Sg after chemical isolation in the gas-phase was established by directly identifying the nuclides ^{265}Sg and ^{266}Sg via the observation of their characteristic, genetically linked, nuclear decay chains [30]. Also, a first thermochemical property of Sg, namely the adsorption enthalpy of Sg oxochloride on the chromatographic surface was measured in these experiments [31]. More recently, Sg was also characterized as volatile oxide hydroxide in on-line isothermal chromatography experiments [32].

4.1 VOLATILE COMPOUNDS OF SEBORGIUM

4.1.1 *Halides and Oxohalides*

Of the hexahalides the compounds MF_6 (M = Mo, W), WCl_6 and WBr_6 are known. $MoCl_6$ is not stable and exists probably only in the gas phase in chlorine atmosphere. WCl_6 can be volatilized to a monomeric vapor while WBr_6 is decomposing to WBr_5 on moderate heating. Of the pentahalides the pentafluorides and the pentachlorides are known, W also forms the pentabromide. While MoF_5 and WF_5 have the typical tetrameric structure of the pentafluorides, $MoCl_5$ and WCl_5 form dimeric species in the solid. $MoCl_5$ is monomeric in the gas phase.

In contrast to the pure halides the oxohalides of group 6 elements are more stable and show a similarly high volatility. For the oxidation state +6 the two stoichiometric types MOX_4 and MO_2X_2 (M = Mo, W; X = F, Cl) exist. The Mo compounds are less stable than those of W. Of the oxofluorides $MoOF_4$, MoO_2F_2, and WOF_4 are known, whereas the existence of WO_2F_2 is doubtful. Of the oxochlorides all four species exist, however, $MoOCl_4$ decomposes to $MoOCl_3$ already at room temperature. WO_2Cl_2 disproportionates at temperatures above 200°C to form WO_3 and $WOCl_4$. However, there is no indication that single molecules of WO_2Cl_2 are unstable even at elevated temperatures.

In the oxidation state +5 four principal compounds of the type MOX_3 (M=Mo, W; X = Cl, Br) are known. The vapor pressure of Mo and W chlorides and oxochlorides over their respective solids as a function of temperature is shown in Figure 13. The vapor pressure of the pure chlorides $MoCl_5$, WCl_5, and WCl_6 are very similar. The volatility of MoO_2Cl_2 is higher than that of $MoOCl_4$, whereas the situation is reversed for W, where $WOCl_4$ is more volatile than WO_2Cl_2. According to tabulated enthalpies of sublimation, $MoOCl_4$ should be more volatile than MoO_2Cl_2 [33]. This change in the sequence of vapor pressures can be explained by the solid phase entropies.

4.1.2 *Oxides and Oxide Hydroxides*

By analogy to Mo and W the oxides and oxide hydroxides of Sg are expected to be moderately volatile, whereas the heavy actinides and the transactinides Rf and Db do not form volatile oxides and oxide hydroxides. For this reason this class of compounds should be very selective with regard to a gas chromatographic isolation of Sg from the plethora of by-products of the nuclear formation reaction. Mo and W form many stable oxides, but in excess of oxygen the trioxides MO_3 (M = Mo, W) should be the main component. Macroscopic amounts of MoO_3 and WO_3 sublimate preferentially as polymers of the type $(MO_3)_n$. However, carrier-free amounts can be volatilized in dry oxygen only as monomers. In moist oxygen the more volatile oxide hydroxides $MO_2(OH)_2$ (M=Mo, W) can be formed. Extensive studies using thermochromatography and on-line isothermal chromatography [34-36] in dry and moist oxygen have revealed that the transport of Mo and W in moist oxygen is not governed by simple reversible adsorption reactions of $MO_2(OH)_2$, but by a dissociative adsorption according to the reaction

$$MO_2(OH)_2 \leftrightarrows MO_{3(ads)} + H_2O_{(g)} \qquad M = Mo, W$$

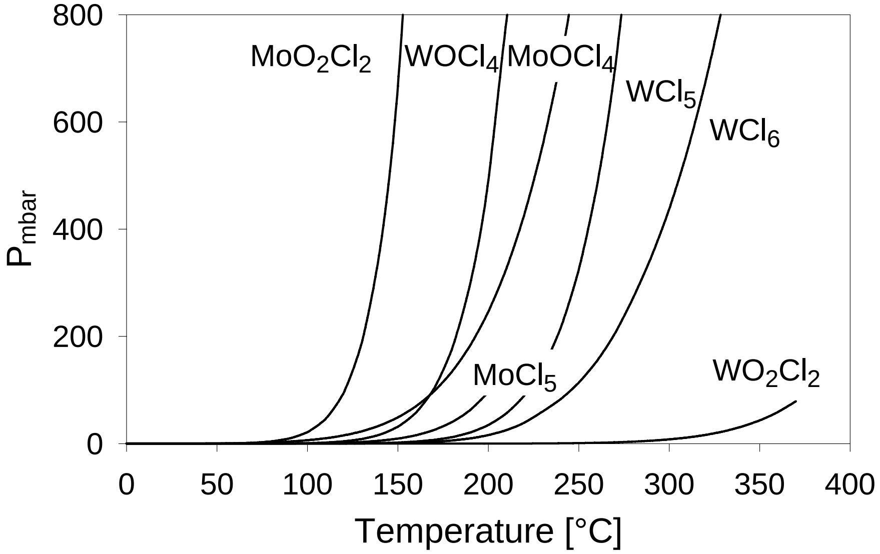

Fig.13. Vapor pressure of Mo and W chlorides and oxochlorides over their respective solids as a function of temperature. $MoCl_5$ is melting at 197°C whereas WO_2Cl_2 disproportionates at temperatures above 200°C. Data from [33].

4.2 GAS CHEMICAL STUDIES WITH SEABORGIUM

4.2.1 *Thermochromatography of Oxochlorides*

Early on, separation procedures to chemically isolate Sg concentrated on inorganic gas chromatography of chlorides and/or oxochlorides [37]. In a number of studies the gas chromatographic behavior of halide and oxohalide species of Mo and W were investigated with respect to a physico-chemical characterization of Sg [38-46]. In experiments by the Dubna group [26-29], the reaction ^{249}Cf (^{18}O, 4n) was employed to produce 0.9 s ^{263}Sg. A very similar set-up as in experiments to chemically identify Rf and Db was used. Reaction products were thermalized behind the target in a rapidly flowing stream of Ar gas and flushed to the adjoining thermochromatography column. Volatile oxochlorides were synthesized by adding air saturated with $SOCl_2$ as reactive agent. The formed oxochloride species migrated downstream the fused silica chromatography column, to which a longitudinal, negative temperature gradient was applied, and finally deposited according to their volatility. In contrast to earlier experiments, no mica plates were inserted, but the fused silica column itself served as sf track detector. The deposition of Sg was registered after completion of the experiment by searching for latent sf tracks left by the sf decay of ^{263}Sg. Indeed, in several experiments a number of sf tracks were found in the column in the temperature region 150 - 250 ºC, which were attributed to the decay of Sg nuclides. Therefore, like its lighter homologs Mo and W, Sg must form volatile oxochloride compounds. The sf tracks were only found, when the quartz wool plug, which was inserted as a filter for aerosols, was absent. This was attributed to the increased surface and thus a much longer retention time. In Figure 14 the location of 41 registered sf events are shown that were observed in the course of three experiments corresponding to a total beam dose of $6.1 \cdot 10^{17}$ ^{18}O beam particles. The dotted histogram shows the data corrected for the relative detection efficiency due to the annealing of fission tracks at elevated temperatures. The solid lines denoted with "[106]" and with ^{176}W show the deposition peak for 2.5 h ^{176}W and the expected shape of the "[106]" deposition peak fitting the sf data. Based on the results of ancillary experiments with short-lived W nuclides, it was concluded that in a first, fast step volatile MO_2Cl_2 (M = W, Sg) molecules are formed and in a second, slower step the deposited MO_2Cl_2 is converted to more volatile $MOCl_4$. Therefore the Sg deposition peak was attributed to the compound SgO_2Cl_2, whereas the ^{176}W deposition peak was attributed to $WOCl_4$. Due to the occurrence of two different species as well as due to the large differences in half-life no information about the relative volatility of MO_2Cl_2 (M = Mo, W, Sg) or $MOCl_4$ (M = Mo, W, Sg) within group 6 was obtained.

4.2.2 *Isothermal Chromatography of Oxochlorides*

In 1995 and 1996 an international collaboration conducted on-line isothermal chromatography experiments with Sg oxochlorides using the OLGA technique [30, 31]. In this work the longer-lived Sg-isotopes ^{265}Sg and ^{266}Sg were synthesized in the reaction ^{248}Cm (^{22}Ne; 4,5n). Nuclear reaction products, recoiling from the target, were stopped in He gas loaded with carbon aerosols, and — adsorbed to their surface — continuously transported through a thin capillary to the OLGA setup. The aerosols carrying the reaction products were collected on quartz wool inside the reaction oven kept at 1000°C. Reactive gases — Cl_2 saturated with $SOCl_2$ and traces of O_2 — were introduced in order to form volatile oxochlorides (thermodynamic calculations [45] indicate that Mo and W most probably form the dioxide dichloride MO_2Cl_2, M = Mo, W). Simultaneously, the carbon aerosols were converted to CO_2. The chromatographic separation takes place downstream in the adjoining isothermal section of the column. At temperatures of 300°C and above group 6 oxochloride molecules travel through the column essentially without delay.

In a first experiment conducted at isothermal temperatures of the chromatography column of 300°C and 400°C the nuclide ^{265}Sg was unambiguously identified after chemical isolation by the observation of its α-decay chains [30].In a second experiment at 350°C isothermal temperature, the results of the first experiment were confirmed by observing further ^{265}Sg α-decay chains [47]. Without changing any of the other experimental parameters, the isothermal temperature was then lowered to 250°C and the yield of ^{265}Sg was measured with a comparable sensitivity as at higher isothermal temperatures. In order to assure that the experimental set-up performed as expected, the nuclide ^{168}W was simultaneously produced from a small ^{152}Gd admixture to the ^{248}Cm target material and its yield was monitored. In Figure 15, the relative yields measured for oxochlorides of short-lived Mo, W, and Sg nuclides are shown as a function of isothermal temperature (the Sg data points measured at 300°C, 350°C and 400°C are summarized in one data point). The yield curve for ^{168}W was measured with the same chromatography column and under the same experimental conditions as they were then used for the isolation of Sg, whereas the yield curve for ^{104}Mo was determined in an earlier measurement. The solid lines show the results of a Monte Carlo simulation procedure where the migration of a molecule through the chromatography column has been modeled [48]. From the measured Sg data thermochemical properties of a Sg compound could be deduced. The sequence in volatility of MO_2Cl_2 (M = Mo, W, Sg) on the stationary phase is $MoO_2Cl_2 > WO_2Cl_2 \approx SgO_2Cl_2$. The probability that SgO_2Cl_2 is equally or even more volatile than MoO_2Cl_2 was estimated to be less than 15%.

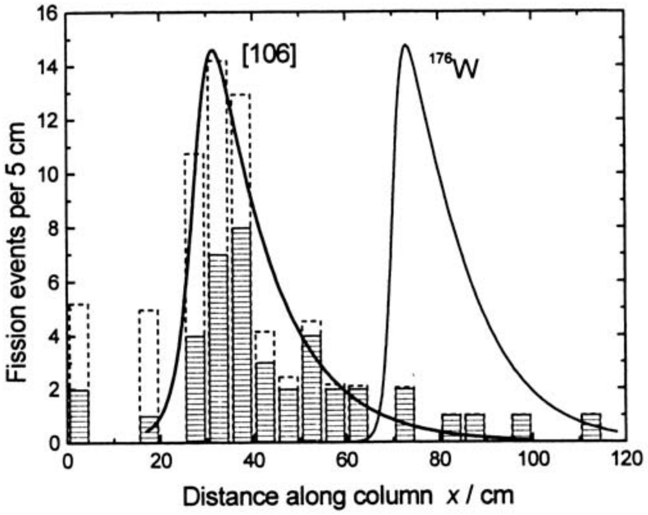

Fig.14. Measured distribution of spontaneous fission events attributed to the decay of an isotope of element 106 (Sg). The dotted histogram shows the data corrected for the relative detection efficiency due to annealing of fission tracks. The thick solid curves show the smoothed corrected thermochromatograms for Sg and ^{176}W. Figure reproduced from [29].

Using an empirical correlation between the experimentally determined ΔH_a^0-values with their macroscopic sublimation enthalpies (ΔH_s^0) it was possible to estimate $\Delta H_s^0(SgO_2Cl_2)=127^{+10}_{-21}$ kJ/mol. $\Delta H_s^0(SgO_2Cl_2)$ is a very important quantity to estimate e.g. ΔH_s^0(Sg). Seaborgium is expected to have an equally or even higher ΔH_s^0 than W, the least volatile element in the Periodic Table.

4.2.3 *Isothermal Chromatography of Sg Oxides/Oxide Hydroxides*

Since the transport of group 6 elements Mo, W, and presumably also Sg in moist oxygen containing gases occurs via a dissociative adsorption reaction and not via a simple reversible adsorption, the retention times in an isothermal chromatography column are generally longer, also at very high temperatures. With the **Hi**gh **T**emperature On-Line **G**as Chromatography **A**pparatu**s** (HITGAS) [49] retention times of about 8 to 9 s were determined from measurements with short-lived Mo- and W nuclides at isothermal temperatures above 1270 K. Therefore, in experiments to characterize Sg as oxide hydroxide, the longer-lived isotope ^{266}Sg ($T_{1/2}\approx 21$ s), produced in the reaction ^{248}Cm (^{22}Ne, 4n) was used despite its lower production cross section of only about 60 pb, compared to the shorter-lived ^{265}Sg ($T_{1/2}=7.4$ s) produced in the 5n evaporation channel with a maximum cross section of about 240 pb [47, 50]. By condensing the separated volatile species directly on metal foils mounted on the circumference of the rotating wheel of the ROMA detection system the time-consuming reclustering step could be avoided.

In an experiment conducted at GSI a ^{248}Cm target was bombarded with 119 MeV ^{22}Ne ions. Reaction products recoiling from the target were stopped in He gas loaded with MoO_3 aerosol particles and swept to the HITGAS set-up. At the entrance to the chromatography column moist O_2 was added to the gas-jet. The temperature of the quartz chromatography column was 1325 K in the reaction and 1300 K in the isothermal zone. A total beam dose of $6.3\cdot 10^{17}$ ^{22}Ne ions was accumulated. The search for genetically linked decay chains $^{266}\mathrm{Sg}\xrightarrow{\alpha}{}^{262}\mathrm{Rf}\xrightarrow{sf}$ revealed two events. The probability that both of these events were entirely random was only 2%. Therefore, as expected, Sg appeared to be volatile under the conditions of the experiment, presumably as Sg oxide hydroxide. In the O_2-$H_2O_{(g)}$/$SiO_{2(s)}$-system Sg showed typical group 6 element properties and also an U(VI)-like behavior, which is also known to form a volatile oxide hydroxide. In Figure 16, the relative yields of Mo and W oxide hydroxides in open quartz columns using humid O_2 as reactive carrier gas component are shown as a function of isothermal temperature. The solid lines are the result of a Monte Carlo model based on a microscopic description of the dissociative adsorption process [35] with $\Delta H^0_{diss.ads}(MoO_2(OH)_2) = -54$ kJ/mol and $\Delta H^0_{diss.ads}(WO_2(OH)_2) = -56$ kJ/mol. The dashed line represents a hypothetical yield curve assuming that group 6 oxide hydroxides are transported by simple reversible adsorption with $\Delta H_a^0=-220$ kJ/mol [32].

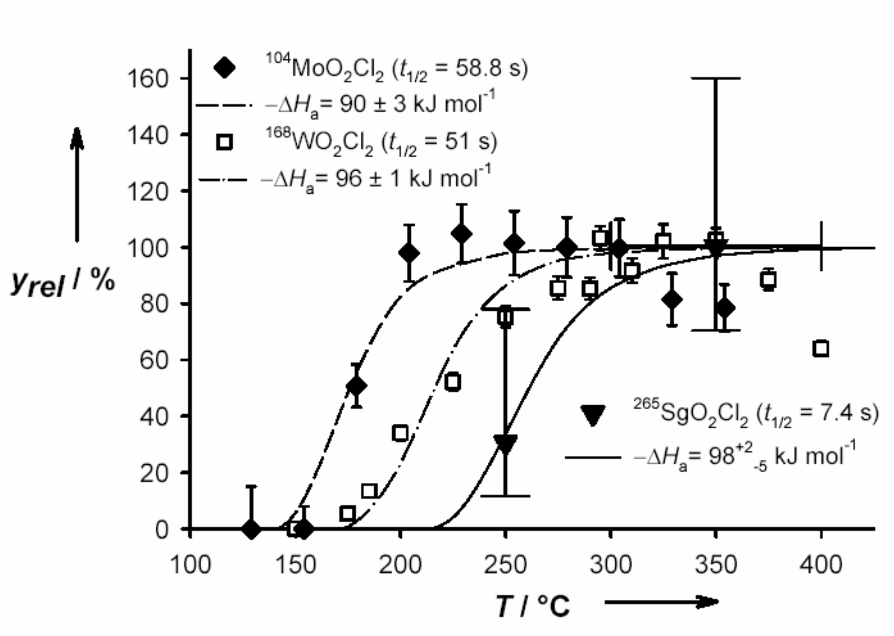

Fig.15. Relative yield of MO_2Cl_2 (M = Mo, W, Sg) as a function of isothermal temperature in the chromatography column Reproduced from [31].

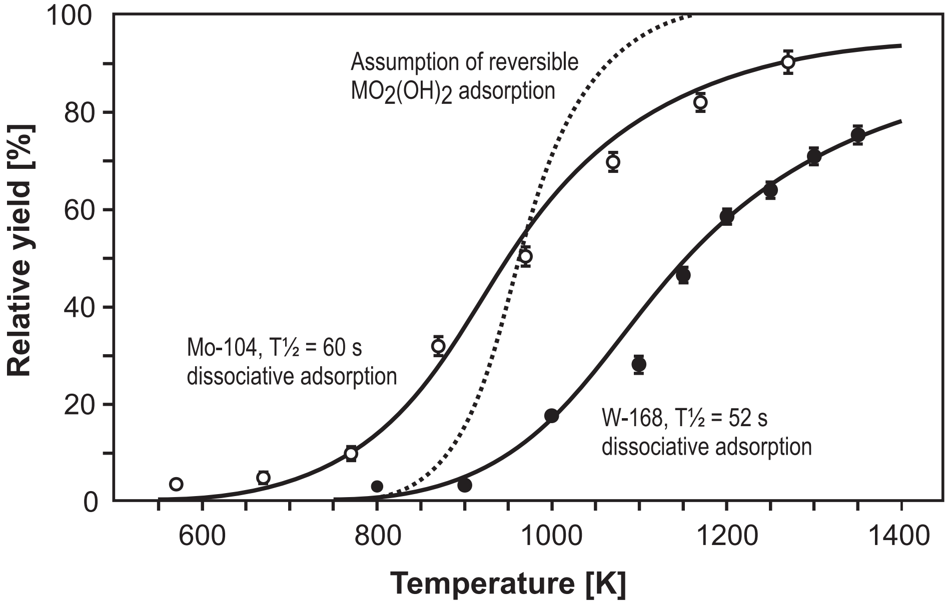

Fig.16. Relative yields in isothermal gas chromatography of ^{104}Mo (○) and ^{168}W (●) oxide hydroxides in quartz columns using humid oxygen as reactive carrier gas component. Two atoms of ^{266}Sg were observed at an isothermal temperature of 1300 K.

In order to answer the question about the sequence of volatility of oxide hydroxides within group 6, additional experiments have to be conducted at lower isothermal temperatures.

5. Bohrium (Bh, Element 107)

The fourth transactinide element bohrium is expected to be homologous to Mn, Tc, and Re and thus to belong to group 7 of the Periodic Table. Two early attempts to chemically identify Bh as volatile oxides or oxide hydroxides failed [51, 52]. For the synthesis of Bh nuclides the reactions ^{249}Bk (^{22}Ne; 4,5n)^{267,266}Bh and ^{254}Es (^{16}O; 4,5n)^{265,266}Bh were employed. The decay properties of the nuclides $^{265-267}$Bh were unknown at the time of these experiments. With the recent identification of the nuclides ^{266}Bh ($T_{1/2} \approx 1$ s) and ^{267}Bh ($T_{1/2} = 17^{+14}_{-6}$ s) [53] in bombardments of ^{249}Bk with ^{22}Ne ions and the recognition that the rapid formation of volatile oxide hydroxides is apparently hindered [54], Eichler et al. [55] paved the way to the first successful chemical identification of Bh as oxochloride compound. However, due to the very low formation cross sections of only about 70 pb for ^{267}Bh produced in the reaction ^{249}Bk(^{22}Ne, 4n) [53], any experiment aiming at a chemical identification of Bh was predestined to be a "tour de force". Nevertheless, in a one month long experiment conducted at Paul Scherrer Institute, Switzerland, an international collaboration of radiochemists observed a total of 6 α-decay chains originating from ^{267}Bh after chemical isolation and established the sequence in volatility $TcO_3Cl > ReO_3Cl > BhO_3Cl$ [56].

5.1 VOLATILE COMPOUNDS OF BOHRIUM

In contrast to groups 4 and 5, but similar to group 6, the 7 valence electrons of group 7 elements allow for a large number of stable oxidation states and thus a wide variety of inorganic compounds. An increased stabilization is observed for the half-filled d-shells, which is especially evident for the 3d shell of Mn, being more volatile than its neighbors Cr and Fe in the same period. However, Mn behaves chemically markedly different from its homologs Tc and Re. Compounds of Mn are chemically most stable in oxidation state +2 whereas compounds in oxidation states +4 and +7 are strong oxidizing agents. Compounds of Tc and Re in high oxidation states are much more stable and the oxidation state +2 is of minor importance. Due to the lanthanide contraction, the atomic and ionic radii of Tc and Re are very similar and thus also their chemical behavior. Some typical mononuclear compounds of group 7 are listed in Table 1. Of all the compounds listed in Table 1 the oxides, oxide hydroxides, and the oxochlorides turned out to be the most promising candidates.

Table 1. Typical mononuclear compounds of group 7 elements

compound	Mn	Tc	Re
oxides	MnO, MnO_2	TcO_2, TcO_3	ReO_2, ReO_3
hydoxides	$MnOH$, $Mn(OH)_2$		
oxide hydroxides		$HTcO_4$	$HReO_4$
sulfides	MnS, MnS_2	TcS_3	ReS_3
halides X = F, Cl, Br, I	MnX_2, MnX_3, MnX_4	TcX_3, TcX_4, TcX_5, TcX_6	ReX_3, ReX_4, ReX_5, ReX_6
oxohalides X = F, Cl, Br, I		$TcOX_3$, $TcOX_4$, TcO_3X	$ReOX_3$, $ReOX_4$, ReO_3X

5.2 GAS CHEMICAL STUDIES OF BOHRIUM

5.2.1 *Thermochromatography of Oxides and/or Oxide Hydroxides*

A first attempt to chemically identify element 107 as eka-rhenium was conducted by Zvara and co-workers already in 1984 [51]. These authors based their separation on the prediction that bohrium should form volatile oxide-hydroxides. As in earlier experiments with Rf, Db and Sg, they searched for latent tracks left by the decay of a spontaneously fissile isotope of Bh in a thermochromatographic column. Moist air with a water vapor pressure of 600 Pa at a flow rate of 0.75 l/min passed behind a 150 μg/cm^2 thick ^{249}Bk target that was irradiated with ^{22}Ne ions. Eight experiments were conducted with varying conditions concerning the operation of the thermochromatographic column. In the last 3 experiments optimum purification from actinides was achieved. No sf-tracks were observed in a temperature range from 800 down 20 °C, while the nuclide ^{177}Re (produced from an admixture of ^{159}Tb to the target material) was adsorbed around 200 °C. This negative result was interpreted that either the half-lives of the produced Bh nuclides were shorter than 2 s or that the production cross sections were lower than 100 pb [51]. Even though the reached cross section limits are very close to the cross sections measured later by Wilk et al. [53], the studies by Eichler et al. [54] showed that the rapid formation of a volatile oxide hydroxide does not take place.

5.2.2 *On-line Gas Chromatography of Oxides*

Later, in a different attempt Schädel et al. [52] bombarded a ^{254}Es target with ^{16}O ions to produce the isotopes ^{266}Bh and ^{265}Bh at the 88-Inch Cyclotron of Lawrence Berkeley Laboratory. Reaction products recoiling from the target were thermalized in He containing 20% O_2 and, attached to the surface of KCl aerosols, transported to the on-line chromatography set-up OLGA. In the reaction oven of OLGA kept at 1050 °C the KCl aerosols were collected on a quartz wool plug. The water content of the gas mixture was kept below 100 ppm in order to form only the trioxide species, as determined in test experiments with Re. Volatile oxides, which passed through the second part of the column with a negative temperature gradient ranging from 1050 °C down to 500 °C at the exit of the column, were deposited on thin Ni catcher foils (0.67 mg/cm^2) that were coated with 50 μg/cm^2 Ta. The catcher foils were mounted on the circumference of a rotating wheel and stepped periodically between pairs of surface barrier detectors to register α- and sf decays. A spectrum of all α-events from all runs (93 MeV and 96 MeV bombarding energy) and all detectors revealed a small portion ($\leq 10^{-3}$) of heavy actinide isotopes that passed through the gas chromatographic column. Even though a couple of α-decays were registered with energies between 8.4 and 9.2 MeV none of these could be conclusively attributed to the decay of a Bh isotope. No genetically linked decay chains were observed. Assuming a transport time of about 1 s and a half-life of the produced Bh isotopes of more than 2 s, cross section limits of about 3 to 10 nb were reached (95% confidence level). These upper limits were larger than the calculated production cross sections by more than one order of magnitude. As outlined by the authors, the experiment clearly failed to chemically identify Bh.

5.2.3 *Isothermal Chromatography of Oxochlorides*

In an experiment at the Philips cyclotron of PSI, the first successful chemical isolation and identification of Bh was accomplished [56]. A target of ^{249}Bk (670 μg/cm^2) covered with a layer of ^{159}Tb (100 μg/cm^2) was prepared at LBNL on a thin (2.77 mg/cm^2) Be foil. The target was irradiated for about four weeks with typically 1.6×10^{12} particles of ^{22}Ne per second at a beam energy in the middle of the target of 119±1 MeV, producing 17-s ^{267}Bh in the reaction ^{249}Bk(^{22}Ne, 4n). ^{176}Re was simultaneously produced in the reaction ^{159}Tb(^{22}Ne, 5n) and served as a yield monitor for the chemical separation process. Nuclear reaction products recoiling from the target were attached to carbon aerosol clusters and transported with the carrier gas flow through a capillary to the modified OLGA III set-up. As reactive gases a mixture of HCl and O_2 was added. After chemical separation final products were attached to CsCl aerosols and transported to the rotating wheel detection system ROMA where α-particle and sf decays were registered in a 4π geometry in a event by event mode. Measurements were performed at isothermal temperatures of 180°C, 150°C, and 75°C, respectively. At each isothermal temperature a beam integral of 10^{18} ^{22}Ne particles was accumulated. A total of 6 genetically linked decay chains attributed to the decay of ^{267}Bh were observed; four at an isothermal temperature of 180°C, two at 150°C and none at 75°C. Due to a small contamination with Po and Bi nuclides, 1.3 of the 4 decay chains observed at 180°C have to be attributed to accidental correlations unrelated to the decay of ^{267}Bh. At 150°C this correction amounted only to 0.1 out of 2 observed decay chains. The properties of the observed decay chains are shown in Figure 17.

Interestingly, at 75°C a relative yield of 80% was observed for ^{169}ReO$_3$Cl compared to 180°C isothermal temperature indicating that BhO$_3$Cl is less volatile than ReO$_3$Cl. The fact that ^{267}Bh was identified after chemical separation already excludes a "Tc-like" behavior of Bh, since CsCl was used as recluster aerosol material, which was not suitable to recluster the very volatile TcO$_3$Cl [57]. The relative yields of the compounds ^{108}TcO$_3$Cl (○), ^{169}ReO$_3$Cl (●), and (most likely) ^{267}BhO$_3$Cl (■) as a function of isothermal temperature are shown in Figure 18. The deduced enthalpies of adsorption on the column surface were $-\Delta H_a{}^0(\mathrm{TcO_3Cl}) = 51\pm3$ kJ/mol, $-\Delta H_a{}^0(\mathrm{ReO_3Cl}) = 61\pm3$ kJ/mol, and $-\Delta H_a{}^0(\mathrm{BhO_3Cl}) = 75^{+6}_{-9}$ kJ/mol (68% confidence interval). Therefore, the sequence in volatility is TcO$_3$Cl>ReO$_3$Cl>BhO$_3$Cl. The probability that BhO$_3$Cl is equally or more volatile than ReO$_3$Cl is less than 10%.

This sequence in volatility agrees well with predictions from fully relativistic density-functional calculations for group 7 oxochlorides that have been performed by Pershina et al. [75]. The results of these calculations have shown that the electronic structure of BhO$_3$Cl is very similar to that of TcO$_3$Cl or ReO$_3$Cl. Increasing dipole moments and electric dipole polarizabilities in the group suggest a decreasing volatility in the sequence TcO$_3$Cl > ReO$_3$Cl > BhO$_3$Cl. However, also classical extrapolations down the groups of the Periodic Table making use of empirical correlations of thermochemical properties predict BhO$_3$Cl to be more stable and less volatile than ReO$_3$Cl or TcO$_3$Cl [76]. As in the case of Sg-oxochlorides the experimentally determined $\Delta H_a{}^0$-value can be used to estimate a macroscopic sublimation enthalpy ($\Delta H_s{}^0$) of BhO$_3$Cl using an empirical linear correlation function. It was therefore possible to directly estimate $\Delta H_s^0(\mathrm{BhO_3Cl}) = 89^{+21}_{-18}$ kJ/mol from only a few investigated molecules.

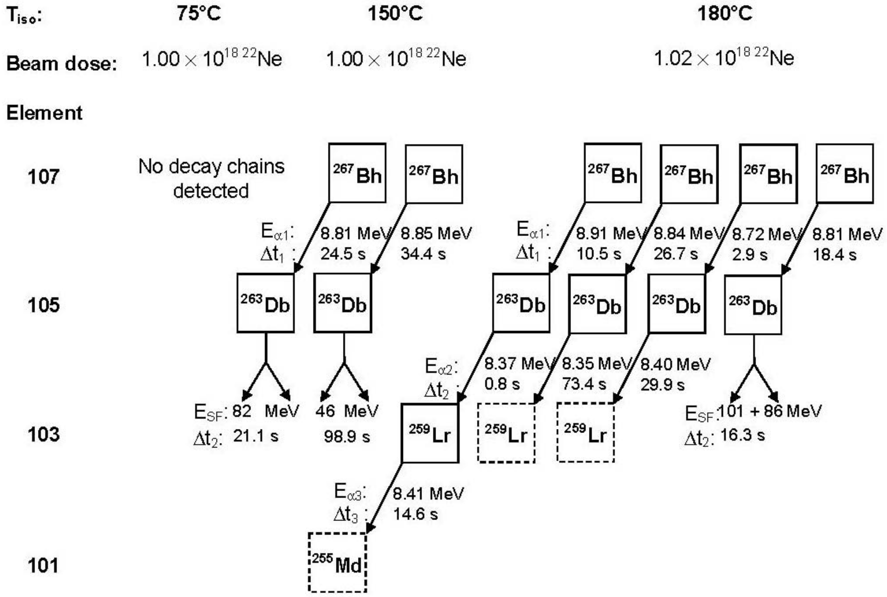

Fig17. The six nuclear decay chains attributed to the decay of ^{267}Bh leading to ^{263}Db and ^{259}Lr. These were observed at 180 °C and 150 °C, which allowed the unambiguous identification of Bh after chemical separation, presumably as volatile $\mathrm{BhO_3Cl}$. No ^{267}Bh was detected at 75 °C isothermal temperature. Figure reproduced from [56].

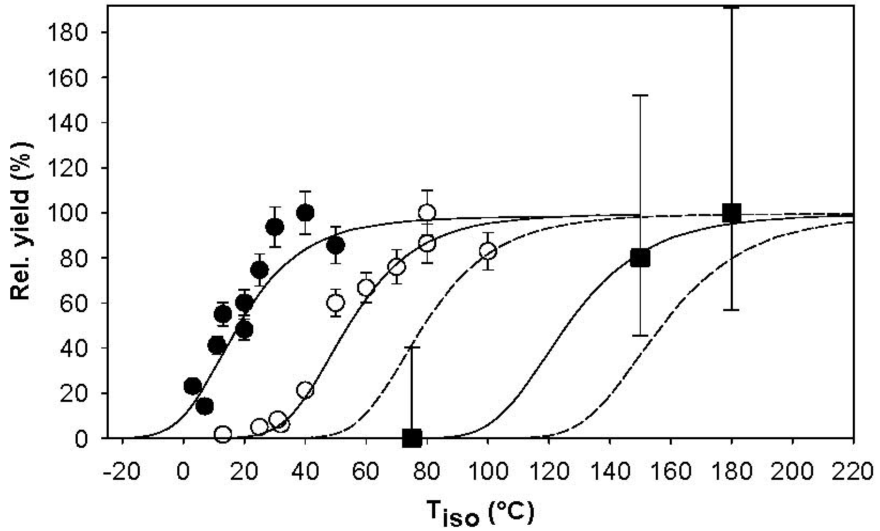

Fig.18. Relative yields of the compounds $^{108}\mathrm{TcO_3Cl}$ (○), $^{169}\mathrm{ReO_3Cl}$ (●), and (most likely) $^{267}\mathrm{BhO_3Cl}$ (■) as a function of isothermal temperature. The error bars indicate a 68% confidence interval. The solid lines indicate the results of simulations with the microscopic model of Zvara [49] with the adsorptionenthalpies given in the text. The dashed lines represent the calculated relative yield concerning the 68% confidence interval of the standard adsorption enthalpyof $\mathrm{BhO_3Cl}$ from -66 to -81 kJ/mol. Figure reproduced from [56].

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6. Hassium (Hs, Element 108)

The experimental chemical investigation and characterization of the next heavier transactinide element Hassium (Hs, element 108) has, for some years, constituted a daunting task even though from the very beginning the selection of a volatile compound was absolutely clear. Hassium, as a presumed member of group 8 of the Periodic Table and thus a homologue of Fe, Ru, and Os, should form stable and at the same time very volatile HsO_4 molecules, very similar to OsO_4. The discovery of Hs was reported in 1984 [77] with the identification of the nuclide ^{265}Hs with a half-life of only 1.5 ms, far too short for all of the currently available chemical separator systems. Only in 1996, the much longer-lived isotope ^{269}Hs with a half-life of the order of about 10 s was observed in the α-decay chain of the nuclide ^{277}112 [78]. However, the production cross section of only about 1 pb for the reaction ^{208}Pb(^{70}Zn, 1n)^{277}112 was discouragingly small. A somewhat larger production cross section of about 7 pb could be expected for the direct production of ^{269}Hs in the reaction ^{248}Cm (^{26}Mg, 5n) [79].

6.1 VOLATILE COMPOUNDS OF HASSIUM

Group 8 elements Fe, Ru and Os are known to exist in a large number of oxidation states: Fe is known in all states from -2 through +6, Ru in the states -2 through +8 (with the exception of +1) and Os in all states from -2 through +8 explaining the large variety of compounds. Ru and Os are the elements with the highest maximum valency within their periods and the only elements which can form an 8^+ oxidation state (with the exception of Xe, which is known to form tetrahedral XeO_4 [81]). While the chemistry of Ru and Os is quite similar, Fe behaves differently. The reason is the existence of the lanthanide series which is inserted in the sixth period of the Periodic Table. Therefore, investigations of the chemical properties for a future Hs chemistry experiment concentrated on Ru and Os. The most important volatile compounds of Ru and Os are the tetroxides MO_4 (M=Ru, Os). There also exist a number of volatile Ru- and Os halides and oxohalides. The fluorides and oxofluorides are of importance, but experimentally difficult to handle. Quite naturally, early considerations [82, 83] and experimental developments [84-97] for a first Hs chemistry exclusively concentrated on the tetroxides. This strategy is justified, since classical extrapolations [98] as well as fully relativistic density functional theory calculations on the group 8 tetroxides [99] predict the existence of a volatile and very stable HsO_4.

6.2 EARLY ATTEMPTS TO CHEMICALLY IDENTIFY HASSIUM

A first unsuccessful attempt to chemically identify Hs as volatile HsO_4 was reported by Zhuikov et al. [89] from Dubna. The reaction ^{40}Ar+^{235}U was employed to produce short-lived α-decaying isotopes of element 110 and Hs daughter nuclides which might be detected by their sf-decay. Atoms recoiling from the target were stopped in air and transported to a thermochromatography column, where the purification from actinides took place on a hot quartz wool filter. OsO_4 was adsorbed quantitatively on Lavsan (polyethylenphtalat) fission track detectors covered with 50 µg/cm^2 of Pb. No sf decays were registered resulting in a production cross section limit of 10 pb for nuclides with half-lives longer than 150 ms.

In a second experiment, using the reaction ^{249}Cf (^{22}Ne, 4n)^{267}Hs, Zhuikov et al. [89] searched also for short-lived α-particle emitting isotopes of Hs. Recoiling atoms were thermalized in a mixture of Ar + 2% O_2 and continuously swept from the target chamber through a Teflon capillary to a quartz column kept at 1000-1100 °C filled with CaO to retain non-volatile nuclear reaction products i.e. actinides, Ra, Fr, and Po. Volatile species were then transported through a Teflon capillary and blown onto the surface of a Si detector covered with 50 $\mu g/cm^2$ of Pb. At the opposite side an annular Lavsan track detector (also coated with 50 $\mu g/cm^2$ of Pb) was located for registering fission fragments. The whole counting device was placed inside a shielding of Cd and paraffin in order to decrease the background. In model experiments with Os, OsO_4 was efficiently absorbed on the Pb surfaces. The decontamination from actinides was excellent (separation factor $>10^6$) as well as that from Po ($>10^3$). Nevertheless, no α-particles in the energy range above 8.5 MeV and no sf events were registered and an upper limit of 100 pb for the production cross sections of α-decaying nuclides with half-lives in the range between 50 ms and 12 h and of 50 pb for spontaneously fissioning nuclides was established.

A similar experiment was reported by Dougan et al. [91]. A set-up called **O**n-line **S**eparation and **C**ondensation **A**ppa**R**atus (OSCAR) was installed at the 88-Inch cyclotron of Lawrence Berkeley Laboratory. Nuclear reaction products were collected with a KCl aerosol gas-jet and transported from the target chamber to the OSCAR set-up where O_2 was added. The aerosol particles were destroyed on a hot quartz wool plug and the formation of tetroxides occurred at a temperature of 650°C. Non volatile reaction products were retained on the quartz wool plug whereas the volatile tetroxides were swept by the carrier gas flow to a condensation chamber, where they were deposited on a Ag disk, which was cooled with liquid N_2. An annular Si surface barrier detector registered α-particle and sf decays of nuclides adsorbed on the disk surface. The OSCAR set-up was used to search for α-decaying ^{272}Hs, the expected EC decay daughter of ^{272}Mt (estimated EC-decay half-life: 25 m), produced in the ^{254}Es (^{22}Ne, 4n) reaction. However, no α-decays between 8.7 and 11 MeV were observed and an upper limit for the production cross section of 1 nb was derived.

6.3 ON-LINE THERMOCHROMATOGRAPHY OF HASSIUM

In order to reach the required sensitivity and to obtain at the same time meaningful chemical information about Hs and its compounds different experimental developments had to be combined. First, the most promising approach to synthesize relatively long-lived Hs isotopes appeared to be the reaction ^{248}Cm (^{26}Mg 4,5n)$^{270,269}Hs$. Second, the rate of production could be increased by using an intense ^{26}Mg beam impinging on rotating ^{248}Cm targets. Third, the "in-situ" production [96] allowed for highest possible chemical yields of group 8 tetroxides. Fourth, in order to compare the volatility of HsO_4 with those of its lighter homologues of group 8, thermochromatography is the method of choice since the position of every detected atom contributes chemical information. The only problem of the thermochromatographic technique so far was the unambiguous identification of the decaying nuclide. This problem has been solved by Kirbach et al. [97] who have built a rectangular thermochromatography column consisting of PIN diodes. In the actual Hs experiment an improved version namely the **C**ryo **O**n-**L**ine **D**etector (COLD) was used.

The required gain in sensitivity of one order of magnitude compared to the OLGA set-up used in experiments with Bh was thus accomplished. With the rotating target wheel, synthesis of about 3 atoms of ^{269}Hs per day could be expected, assuming a production cross section of 7 pb. The overall efficiency of the set-up (including detection of a 3 member α-decay chain) amounted to 30 - 50%, resulting in the expected detection of about one decay chain per day of experiment.

In an experiment to produce Hs isotopes conducted in May of 2001 at GSI, of valid data was collected during 64.2 h. During this time 1.0×10^{18} ^{26}Mg beam particles passed through the ^{248}Cm target. Only α-lines originating from ^{211}At, ^{219,220}Rn and their decay products were identified. While ^{211}At and its decay daughter ^{211}Po were deposited mainly in the first two detectors, ^{219,220}Rn and their decay products accumulated in the last three detectors, where the temperature was sufficiently low to partly adsorb Rn. During the experiment, seven correlated decay chains were detected. All decay chains were observed in detectors 2 through 4 and assigned to the decay of either ^{269}Hs or the yet unknown ^{270}Hs. The characteristics of three decay chains agreed well with literature data on ^{269}Hs and its daughter nuclides [78, 100], while two other decay chains were attributed to the decay of ^{270}Hs. The last two decay chains were incomplete and a definite assignment to ^{269}Hs or ^{270}Hs could not be made. No additional three-member decay chains with a total length of $\leq$300 s were registered in detectors 2 to 10. The background count-rate of α-particles with energies between 8.0 and 9.5MeV was about 0.6 h^{-1} per detector, leading to very low probabilities of $\leq 7\times10^{-5}$ and $\leq 2\times10^{-3}$ for any of the first five chains and any of the last two chains, respectively, being of random origin. In addition, four fission fragments with energies >50 MeV that were not correlated with a preceding α-particle were registered in detectors 2 through 4.

The longitudinal distribution of the 7 decay chains originating from Hs is depicted in Figure 19. The maximum of the Hs distribution was found at a temperature of -44 ± 6 °C. The distribution of ^{172}OsO$_4$ ($T_{1/2}$ = 19.2 s) measured before and after the experiment showed a maximum in detector 6 at a deposition temperature of -82 ± 7 °C. As in experiments with lighter transactinide elements the Monte Carlo model of Zvara [19], that describes the microscopic migration of a molecule in a gas chromatographic column, was used to evaluate the adsorption enthalpy of HsO$_4$ and OsO$_4$ on the silicon nitride detector surface. The modeled distributions with $-\Delta H_a^0(\mathrm{HsO_4}) = 46 \pm 2$ kJ/mol (68% confidence interval) and $-\Delta H_a^0(\mathrm{OsO_4}) = 39 \pm 1$ kJ/mol are shown as solid lines in Figure 19.

The higher deposition temperature of about 40 °C and the thus about 7 kJ/mol higher adsorption enthalpy seems to indicate a slightly lower volatility of HsO$_4$ compared to its lighter homolog OsO$_4$. This experimental result was somewhat unexpected since according to both, classical extrapolations and relativistic molecular calculations, HsO$_4$ was predicted to be about as volatile as OsO$_4$. Nevertheless, the high volatility of the Hs oxide species clearly suggests that it is HsO$_4$ since by analogy with the known properties of the Os oxides all other Hs oxides are expected to be much less volatile and unable to reach the detector system. The observed formation of a volatile Hs oxide (very likely HsO_4) provides strong experimental evidence that Hs behaves chemically as an ordinary member of group 8 of the Periodic Table.

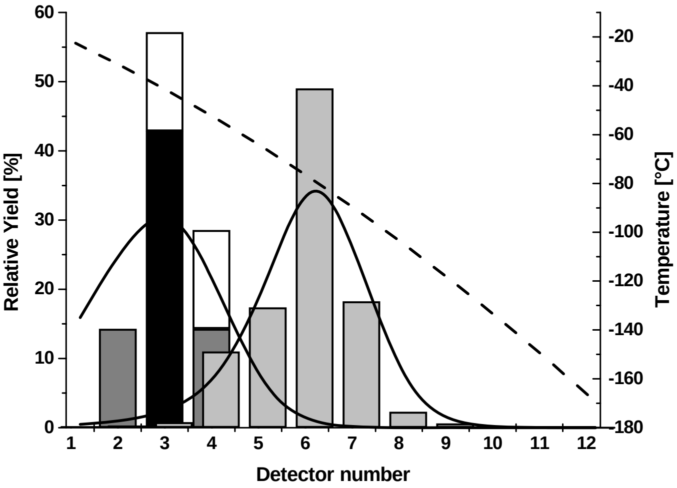

Fig 19. Relative yields of HsO_4 and OsO_4 for each of the 12 detector pairs. Measured values are represented by bars: $^{269}HsO_4$: black; $^{270}HsO_4$: dark grey; $^{269\text{ or }270}HsO_4$: white; $^{172}OsO_4$: light grey. The dashed line indicates the temperature profile (right-hand scale). The maxima of the deposition distributions were evaluated as -44 ± 6 °C for HsO_4 and -82 ± 7 °C for OsO_4. Solid lines represent results of a simulation of the adsorptionprocess with standard adsorption enthalpies of -46.0 kJ/mol for $^{269}HsO_4$ and -39.0 kJ/mol for $^{172}OsO_4$. Figure reproduced from [101].

7. Element 112

From the systematic order of the periodic table element 112 is a representative of group 12 together with zinc, cadmium, and mercury and is expected to have a closed shell electronic ground state configuration $[Rn]5f^{14}6d^{10}7s^2$. Thus, a noble metallic character can be expected. However, relativistic calculations of atomic properties of superheavy elements (SHE) suggest a significant contraction of the spherical 7s- electron orbitals. This may lead to an increased chemical stability of the elemental atomic state for element 112 and a noble-gas like inertness similar to radon. These strongly diverse predictions require experiments able to distinguish between a noble volatile metal and a noble-gas like element. For this purpose the investigation of the gas adsorption properties of element 112 on noble metal surfaces, e.g. gold, was suggested using the same set-up as for the chemical study with hassium but applying Au-covered detectors.

7.1 EARLY SEEMINGLY SUCCESSFUL CHEMISTRY EXPERIMENTS

The first chemical study of this element was very troublesome. A first seemingly successful investigation conducted at FLNR using the reaction $^{48}Ca + ^{238}U$ indicated on the basis of 8 observed events a behaviour different to that of Hg, more like Rn

[110,111]. In this experiment all reaction products were collected in a chamber mounted behind the target and continuously swept by He. Volatile products were then transported along a 30 m long capillary to a semiconductor detector array, where the surfaces were covered by a thin layer of Au, followed by a gas ionisation chamber. All devices were surrounded by neutron counters in order to assay sf-decaying nuclides not only by high-energy events caused by the kinetic energy of the fission fragments but also by the prompt neutrons emitted during the fission process. (Fig. 20).

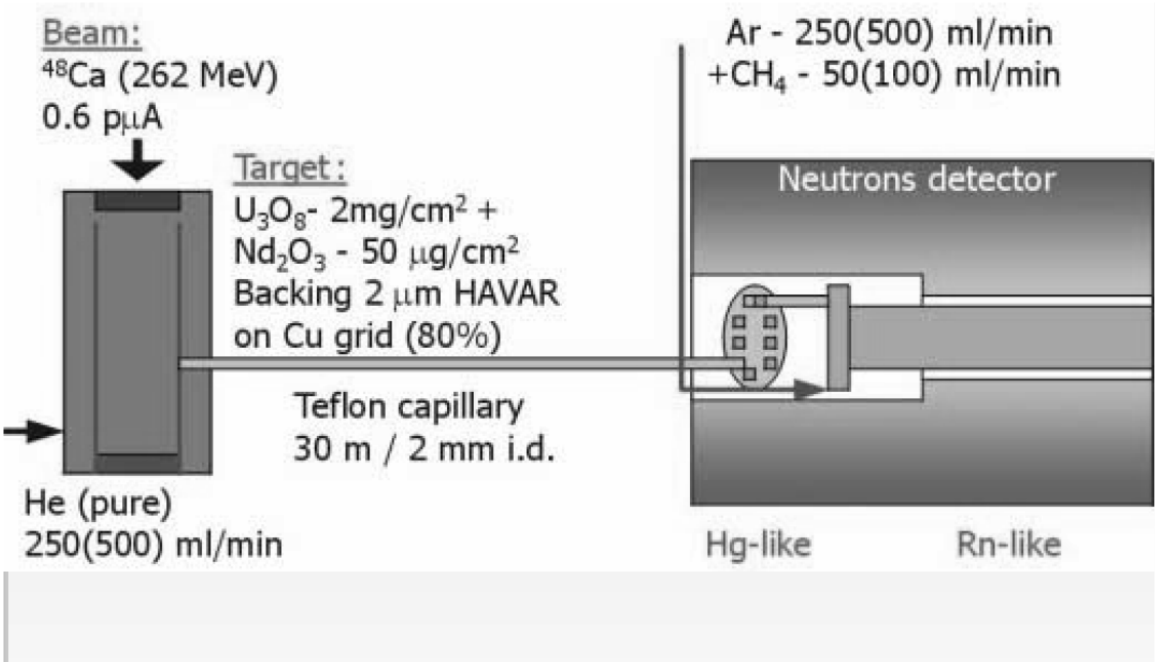

Fig. 20: Set-up used in the first experiment with element 112 at FLNR. Reproduced in modified version from. [111])

Products like Hg were quantitatively adsorbed on the semiconductor surface while noble gases like Rn were transported to the ionization chamber. All 8 events were detected in the gas ionization chamber. It was concluded that element 112 is “Rn-like”.

This observation was corroborated by a second experiment at GSI [112] that used the same set-up as for the experiments with Hs (see above), except that the detector surfaces were covered by a thin Au layer. In the same ^{48}Ca + ^{238}U reaction several sf events were found at very low temperatures, where adsorption of Rn was observed.

All these experiments suffered from the fact that only sf decay was used to identify final products, assuming the isotope ^{283}112 to be a long-lived nuclide decaying via spontaneous fission with several minutes half-life. This information came from physics experiments [102, 103]. Both chemistry experiments, however, pointed to a weak aspect: the fission fragment energies observed were far below expectations. Several arguments tried to explain this mismatch. Therefore, these experimental observations required confirmation by improved set-ups.

Later, additional physics experiments proved that the nuclide ^{283}112 is much shorter-lived, having a half-life of only 4 s and decaying by α-emission and not by sf [113]. It soon became clear that the first chemical studies were too slow (separation times approx. 0.5 min) to be able to detect such a short-lived product. This new situation asked for chemistry experiments with shorter separation times of a few seconds.

7.2 RECENT THERMOCHROMATOGRAPHY EXPERIMENTS

In two experiments using the ^{48}Ca + ^{238}U reaction with a total beam dose of $5.9\text{x}10^{18}$ again no indication for element 112 (i.e. ^{283}112) was found at a cross section limit of 1.3 pb (2σ conf. level) [114] even though a fast transport system with a separation time of approx. 4 s was used. This limit, however, was within error not in disagreement with the cross section claimed for this reaction from the Dubna physics experiments ($2.5^{+1.8}_{-1.1}$ pb) and from the GSI physics experiments ($0.7^{+0.6}_{-0.4}$ pb) [115]. It was then decided to produce element 112 in an "overshoot" reaction, where the evaporation residue is much shorter-lived than the separation time of the set-up and where the decay product is element 112. The choice was ^{48}Ca + ^{242}Pu, because in the 3n evaporation channel the 0.5 s ^{287}114 nuclide is formed with 4 pb cross section. This nuclide decays by α-emission to the 4s- ^{283}112 [113].

Indeed in the course of a three week bombardment (beam dose: $3.1\text{x}10^{18}$) two genetically linked α-sf decay chains were detected [116]. The observed two sf decays were the only sf fragments measured throughout the entire experiment. The coincident detection of both sf fragments revealed a total kinetic energy of about 230 MeV, which is typical for the sf decay of a very heavy nucleus. The correlation of both observed sf events to single high energy alpha decays in the same detector within the preceding 0.6 s renders these measured decay chains having an exceptionally low probability to be of random origin. This experiment was repeated with the same beam dose and three additional decay chains from ^{283}112 were found [117]. All decay chains are depicted in Fig. 21. They agree well with the data from the physics experiments [113].

Identification of these five atoms occurred in an array consisting of 32 pairs of PIPS detectors along which a temperature gradient was established between -20 °C (later +35°C) and approx. -185 °C, respectively. In the first part of the first experiment, the temperature at the entrance of the Au covered detector array was -20 °C. The first event was detected close to the entrance of this array at -24°C. This means that the "true" deposition temperature should be -24°C or higher. In the second part of the first experiment the temperature at the entrance of the detector array was increased to +35 °C, the highest value at which counting with semiconductor detectors is still possible. The second atom was the found at -5 °C. In the second experiment the gas flow rate was nearly doubled from 0.8 L/min to 1.5 L/min in order to reduce the transport time from the collecting chamber to the detector array from 4s to 2s. As expected from Monte Carlo modelling, the three additional atoms were observed at lower temperatures of -21 °C and -39°C, respectively and on the ice layer at – 121 °C. Under the given gas purity conditions, a tiny ice layer formed on the surface of the detectors at temperatures below -95 °C. The four atoms observed on the Au surface can be consistently described with one adsorption enthalpy of -52^{+20}_{-4} kJ/Mol.

Applying an empirical correlation between adsorption enthalpies of s- and p-elements on Au at ultra-trace level with their respective sublimation enthalpies (Figure 22) yields a sublimation enthalpy for element 112 of 39^{+23}_{-10} kJ/mol. This value is in line with extrapolation within group 12 (Fig. 23). It clearly points to a still metallic and not to a noble gas like behaviour of element 112, in line with theoretical expectations [105, 118,119]. Therefore, the closed $7s^2$ shell still enables the $6d^{10}$ electrons to have a metallic bonding character.

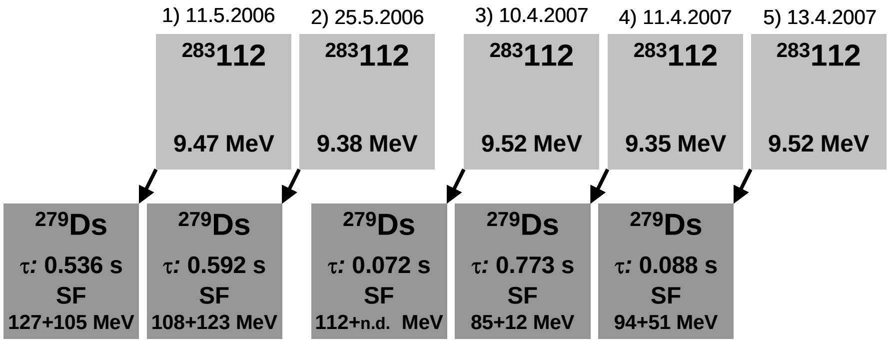

Fig 21: Decay chains form element 112 observed in two chemistry experiments performed in 2006 and 2007 at FLNR from the ^{48}Ca + ^{242}Pu reaction at a total beam dose of $6.2x10^{18}$ (data from [116,117])

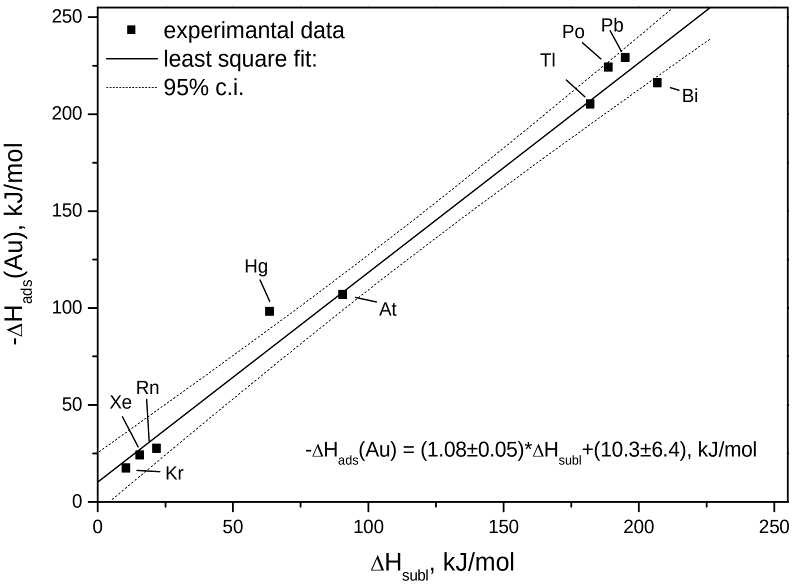

Fig. 22: Empirical correlation between measured adsorption enthalpies of noble gases and of p-elements from the 6th period on Au surfaces at a few-atom level and their respective sublimation enthalpy. Reproduced from [120].

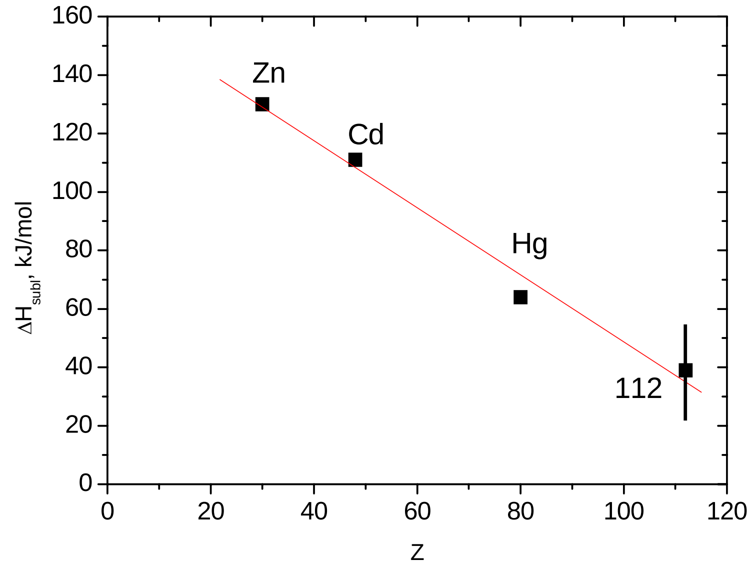

Fig. 23: Sublimation enthalpies for Zn, Cd and Hg from the literature and for element 112 from measured deposition temperatures on Au and a correlation between deduced adsorption enthalpies and sublimation enthalpies.

8. Element 114

With a [Rn]$6d^{10}7s^27p^2$ configuration the question was how the filled $7p_{1/2}$ subshell influences the chemical properties of element 114. Due to a pronounced spin-orbit splitting between the spherical $7p_{1/2}$ and distorted $7p_{3/2}$ orbitals estimates ranged from a noble gas-like behaviour [106] to a lead-like behaviour [107]. Since currently no gas chemistry device would be able to cover such a broad range of volatilities, it was decided to first search for a very volatile element 114 using the same set-up as applied in the chemistry experiments with element 112.

This experiment was conducted in 2007 at FLNR. In the course of two experiments using the reactions ^{48}Ca + ^{242}Pu and ^{48}Ca + ^{244}Pu three decay chains assigned to element 114 were observed, with low probability to be of random origin, one of 0.5s ^{287}114, and two of 0.8 s ^{288}114. This result was somewhat surprising given the transport time of 2 s.

Two of the three atoms were observed on the Au surface at very low temperatures, between -80 and -90 °C, where adsorption of heavy noble gases via *van der Waals* interaction is expected. This finding is in line with expectation from Pitzer [106] but disagrees with more recent predictions. Semi-empirical extrapolations [121] and relativistic theoretical calculations [122] predict element 114 to behave like a volatile metal, slightly more volatile than Pb but certainly not like a noble gas. Therefore, these experiments will be continued in 2008 to search for additional atoms of element 114.

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