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THE CHEMISTRY OF SUPERHEAVY ELEMENTS

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Dedicated to Adam Sobiczewski in honour of his 70th birthday

The chemistry of transactinide or superheavy elements has reached element 108. Preparations are under way to leap to element 112 and beyond. The current status of this atom-at-a-time chemical research and its future perspectives are reviewed from an experimental point of view together with some of the interesting results from n-rich nuclides near and at the N=162 neutron shell. Experimental techniques and important results enlightening typical chemical properties of elements 104 through 108 are presented in an exemplary way. From the results of these experiments it is justified to place these elements in the Periodic Table of the Elements into groups 4 through 8, respectively. However, mainly due to the influence of relativistic effects, it is no longer possible to deduce detailed chemical properties of these superheavy elements simply from this position.

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1. Introduction

The first scientifically sound mentioning of the possible existence of nuclei dubbed "superheavy" [1,2] was accompanied by a discussion about a nuclear shell-closure at $Z = 126$, see *e.g.* [3]. Soon, theoretical calculations began to focus on the $Z = 114$ and $N = 184$ nucleus for the center of superheavy elements with contributions by Sobiczewski *et al.* [4], and by Meldner [5] and many others during a conference [6] in 1966. First half-life estimates, see *e.g.* [7–11], yielded times which were encouraging for chemistry experiments to search for and to investigate superheavy elements, SHE. Also neighboring odd-Z elements were considered [12].

At about the same time Dirac–Fock and Dirac–Fock–Slater calculations were performed for atoms to determine the electronic structure of superheavy elements [13–18]. These results, which are summarized in [19], show that, to some extent, extrapolations of chemical properties along groups of elements in the Periodic Table should be a valid approach to estimate chemical properties of superheavy elements. However, this was also the time when from the above calculations the importance of a relativistic treatment of the electronic orbitals was recognized. Several authors discussed relativistic effects on chemical properties which may result in unexpected chemical properties, see *e.g.* [20–23] and references therein. Only over the last decade a theoretical breakthrough towards theoretical predictions of chemical properties was achieved with the development of relativistic quantum molecular theories; for reviews see [24, 25].

Today we know of 112 chemical elements [26]. The discoveries of elements 114 [27–29] and 116 [30, 31] are currently waiting to be confirmed. Element 104, rutherfordium, Rf, marks the beginning of a remarkable series of chemical elements: From a nuclear point of view they can be called superheavy elements — as they only live because of their microscopic shell stabilization (see below for a detailed discussion of this aspect) — and from a chemical point of view they are transactinide elements — as the series of actinides ends with element 103 [32]. One of the most important and most interesting questions for a chemist is the one about the position of superheavy elements in the Periodic Table of the Elements; see Fig. 1.

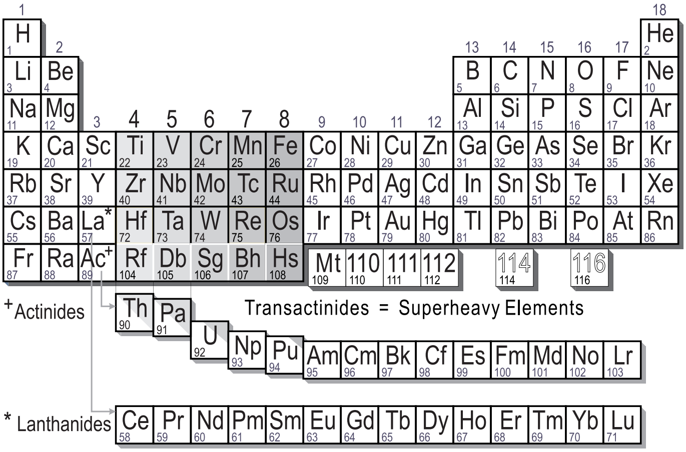

Fig. 1. Periodic Table of the Elements. The known transactinide elements 104 through 112 shall take the positions of the seventh period transition metals below Hf in group 4 and Hg in group 12. While chemical studies have justified placing the elements Rf through Hs into the Periodic Table, the "chemically unknown" heavier elements still need to be investigated. The arrangement of the actinides reflects that the first actinide elements still resemble, to a decreasing extent, the chemistry of d-elements: Th below group 4 elements Zr and Hf, Pa below Nb and Ta, and U below the group 6 elements Mo and W.

From atomic calculations, see *e.g.* [13,24], one expects that the filling of the 6d electron shell coincides with the beginning of the series of transactinide elements. Consequently, a chemical behavior similar to the one known from the lighter transition metals in the fifth and sixth periods can be anticipated. However, it is by no means trivial to put rutherfordium into group 4 of the Periodic Table — and the heavier ones into successive groups — if one accepts that the Periodic Table as an ordering scheme also reflects the chemical property of an element at a given position.

Modern relativistic atomic and molecular calculations [24] clearly show the very large influence of direct and indirect relativistic effects on the energetic position and the sequence of electrons in their respective orbitals. This is also associated with changes in their radial distributions. All these changes are so pronounced that, if compared with non-relativistic calculations, significantly different chemical properties for SHE would not be surprising. Therefore, it is of great interest to study chemical properties of SHE in detail and to compare these with properties deduced from extrapolations and from modern relativistic molecular calculations in combination with empirical models. First generation experiments on rutherfordium [33–35] and element 105, dubnium, Db, [36,37] rendered enough justification to place Rf into group 4 and Db into group 5 of the Periodic Table.

The chemistry of SHE, or transactinide elements, has now reached element 108. First experiments are under way to reach out for element 112 and beyond. These experiments have concentrated on the question how the chemical properties of SHE compare with the ones of their respective lighter homologues and how well the Periodic Table accommodates the transactinide elements as transition metals in the seventh period.

This contribution is focusing *(i)* on some key experiments to unravel detailed chemical properties of elements 104 and 105 in the liquid phase and in the gas phase, *(ii)* on first survey experiments of element 106, seaborgium, Sg, and *(iii)* on the first, successful experiments on element 107, bohrium, Bh, and on element 108, hassium, Hs, performed in the gas phase. It includes aspects of nuclear reactions and nuclear decay in an exemplary way, experimental techniques, important experimental results enlightening the chemical properties of these elements, and perspectives. For comprehensive reviews of earlier and additional results, especially on the Rf, Db and Sg chemistry, see, *e.g.*, Refs [38–41].

2. Nuclear aspects

2.1. The region of superheavy elements

Characteristic electronic and chemical properties allow locating the beginning of the transactinide elements at element 104 — but where do SHE begin? Until the early 80's a straight forward answer would have pointed towards the remote "island of stability" centered at $Z = 114$ and $N = 184$ which was surrounded by a "sea of instability" [42]. Based upon experimental results [26, 43, 44] and theoretical concepts, which take into account shell-stabilized deformed nuclei and emphasize the importance of the N=162 neutron shell [45–51], we know that the sea of instability has drained and that sandbanks and rocky footpaths are connecting the region of shell-stabilized spherical nuclei to our known world.

Perfectly acceptable, some authors are still using the term SHE in connection with spherical nuclei only. However, others have widened this region and have included lighter elements as, *e.g.*, already discussed in the article by Sobiczewski, Patyk and Cwiok entitled *Do the Superheavy Nuclei Really Form an Island?* [47]. In the following, an argument is developed to show that it may be well justified to begin the superheavy elements with element 104. The results is especially appealing as the beginning of SHE coincides with the beginning of the transactinide elements.

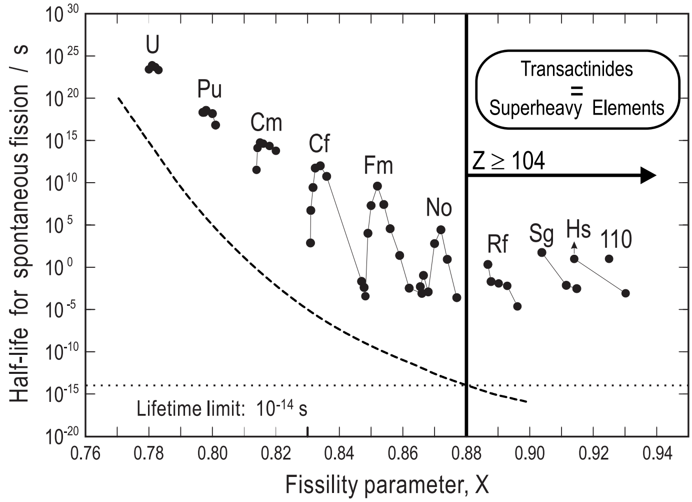

Fig. 2. Known spontaneous fission half-lives of even-even nuclides (dots) and calculated hypothetical half-lives taking into account the liquid drop part only (dashed line) plotted versus the fissility parameter. The dotted line shows the 10^{-14} s lifetime limit for a chemical element. After [55, 56] with additional data from [29, 60–62].

Two definitions or assumptions are used: *(i)* Superheavy elements is a synonym for elements which only exist due to their nuclear shell effect. *(ii)* Following arguments given in Reference [52] only those composite nuclear systems that live at least 10^{-14} s shall be considered a chemical element. This time is well justified from nuclear aspects, *e.g.* from maximum lifetimes of excited compound nuclei, as well as from chemical aspects, *e.g.* from the minimum formation time of a molecule [53]. Applying these two assumptions to a comparison of experimentally observed spontaneous fission half-lives and calculated ones using the macroscopic liquid-drop part only, see [54–56] for more details, yields a fissility parameter of 0.88 at which hypothetical "liquid drop half-lives" drop below the 10^{-14} s margin while the shell contribution allows these nuclides to live up to factors of about 10^{15} longer; see Fig. 2. From this one can state that all elements beginning with element 104 — the transactinides — live only because of their microscopic shell stabilization and, therefore, shall be called superheavy elements.

2.2. Nuclear syntheses

Actinide target based heavy-ion reactions, frequently termed "hot-fusion" reactions, are applied to synthesize the most neutron-rich and relatively long-lived isotopes needed in chemical investigations of SHE. Half-lives, nuclear reaction syntheses and cross sections are summarized in Table I [57]. More

TABLE I

Nuclides from "hot-fusion" nuclear reactions used in SHE chemistry. From [57].

Nuclide	$T_{1/2}$	Target	Beam	Evap.	σ	Prod. rate$^{(c)}$
^{261m}Rf	78 s	^{248}Cm (a)	^{18}O	5n	≈10 nb	2 min^{-1}
		^{244}Pu (b)	^{22}Ne	5n	4 nb	1 min^{-1}
^{262}Db	34 s	^{249}Bk (a)	^{18}O	5n	6 nb	2 min^{-1}
		^{248}Cm (b)	^{19}F	5n	1 nb	0.5 min^{-1}
^{263}Db	27 s	^{249}Bk (b)	^{18}O	4n	10 nb	3 min^{-1}
^{265}Sg	7.4 s	^{248}Cm (a)	^{22}Ne	5n	≈240 pb	5 h^{-1}
^{266}Sg	21 s	^{248}Cm (b)	^{22}Ne	4n	≈25 pb	0.5 h^{-1}
^{267}Bh	17 s	^{249}Bk (a)	^{22}Ne	4n	≈70 pb	1.5 h^{-1}
^{269}Hs	14 s	^{248}Cm (a)	^{26}Mg	5n	≈6 pb	3 d^{-1}
^{270}Hs	2-7 s	^{248}Cm (b)	^{26}Mg	4n	≈4 pb	2 d^{-1}

(a) Reaction commonly used in chemistry experiments.

(b) Reaction occasionally used or nuclide observed as a "by-product".

(c) Assuming typical values of 0.8 mg/cm^2 for the target thickness and beam intensities of 3×10^{12} particles per second.

detailed discussions about specific aspects of hot fusion reactions can be found in [43, 58, 59]. Cross sections for the syntheses of n-rich, light transactinides vary from about 10 nb to a few pb. With typical beam intensities of 3×10^{12} heavy ions per second on targets of about 0.8 $\mathrm{mg}\times\mathrm{cm}^{-2}$ thickness production yields range from a few atoms per minute for Rf and Db isotopes to five atoms per hour for ^{265}Sg [60], to some tens atoms per day for ^{267}Bh [63, 64] and a few atoms per day for ^{269}Hs [61, 62]. Therefore, all chemical separations are performed with single atoms on an "atom-at-a-time" scale. Similar to the experiments with recoil separators characteristic α-decays and time correlated α–α-decay chains are used to identify these nuclides in specific chemical fractions or at characteristic positions after chemical separation.

2.3. Nuclear decay

As nuclear chemistry techniques, see Section 3, are not only highly efficient to collect products from "hot-fusion" and from multi-nucleon transfer reactions but also well adapted to half-lives of a few seconds and longer it is not surprising that many of the longer-lived, most n-rich isotopes of the heaviest actinides and early transactinides were discovered or first studied applying these techniques. In the following a few examples of "nuclear results" are given that were obtained in the course of the chemistry experiments discussed in Section 4.

Early attempts to identify the $4n$-evaporation residue of the ^{18}O on ^{249}Bk reaction without chemical separation remained unsuccessful [65, 66] because of a too high background from unwanted but unavoidable nuclear reaction products. Chemically separating an element 105 fraction within about 3 s [67] gave access to the discovery and first investigation of this most n-rich dubnium isotope ^{263}Db [67, 68]. ^{263}Db was found to decay by spontaneous fission ($57^{+13}_{-15}\%$) and by α emission (E_α=8.35 MeV) with a half-life of 27^{+10}_{-7} s. The spontaneous fission energy spectrum was compatible with an average total kinetic energy of about 207±7 MeV. As a result of this observation not only previously determined cross section values but also decay properties of ^{262}Db had to be revised [67, 68] because of ^{263}Db contributions in earlier ^{262}Db measurements.

A series of chemical investigations of element 106 yielded, in addition to many chemical results, valuable information on the decay of ^{265}Sg and ^{266}Sg [60, 69] from the observation of time correlated α–α–(α) and α-SF decay chains. A half-life of $7.4^{+3.3}_{-2.7}$ s was determined for ^{265}Sg and 21^{+20}_{-12} s for ^{266}Sg. Among other nuclear decay information, upper limits for SF of $\leq$35% and $\leq$82% were established for ^{265}Sg and ^{266}Sg, respectively. Using the lower error limit of the half-life of ^{266}Sg a lower limit for the partial

SF half-life of $T^{SF}_{1/2}(^{266}Sg) \geq 11$ s was determined for ^{266}Sg. In very good agreement with theoretical calculations [50] this result was one of the first experimental observations of the stability of the N=162 neutron shell.

The first chemical study of element 108 [61], produced in the reaction of ^{26}Mg with ^{248}Cm at the GSI's UNILAC, gave manifold new insights into nuclear aspects of Hs isotopes near and, for the first time, right on the $N = 162$ neutron shell [61, 62]. Of special importance is the evidence for the new proton and neutron shell stabilized nuclide $^{270}_{108}\mathrm{Hs}_{162}$ that shows a strong α-decay branch ($E_\alpha = 9.16$ MeV) and has an estimated half-life of $3.6^{+0.8}_{-1.4}$ s [62]. The estimated Q_α value of 9.30 MeV is in agreement with predictions [48,51]. Assuming an upper limit SF branch of about 50%, which would not be in contradiction with the experimental results, a partial lower-limit SF half-life of about 10 s would result while theory predicts 1.8 h [50].

New information was gained on the decay of ^{261}Rf observed as the granddaughter in α–α-decay chains originating from ^{269}Hs. There is good evidence that the so-far believed 78-s ground state of ^{261}Rf is an isomeric state and that the ^{261}Rf ground-state decay energy is 8.52 MeV and has a half-life of 7.3 s. Moreover a SF branch of about 33% is calculated for the decay of ^{261}Rf based upon the experimental observation [62]. As an additional result, the observed ^{269}Hs decay chains are in very good agreement with the ^{277}112 decay chain observed in the discovery of element 112 [70], thus independently confirming this element 112 discovery.

3. Experimental techniques for on-line experiments

3.1. Production and transport

The atom-at-a-time situation of chemical separations with transactinides requires an optimization of the following parameters: *(i)* Choice of the nuclear reaction — normally the one with the highest cross section. *(ii)* High production rates — ion-source, accelerator and target technology are cornerstones. *(iii)* Fast transport and fast chemical separation — to avoid severe nuclear decay losses. *(iv)* High yields in transport and in chemical separation. *(v)* Efficient detection and identification. *(vi)* A chemical separation procedure which fulfills these needs and, at the same time, provides the desired information about the chemical behavior of the transactinide element. Many details of various experimental set-ups and detectors are described in [38–40, 71].

A schematic presentation of components for automated on-line experiments with transactinides is shown in Fig. 3. Heavy-ion beams are passing through a vacuum isolation window and target-backing before interacting with the actinide target material. Characteristic to all recent experiments on Rf through Bh was the use of aerosols ("clusters") as the carrier material for nuclear reaction products to be transported in the He-gas jet from the recoil chamber — where they are stopped in the gas — to the chemistry apparatus. Routinely, KCl is used as an aerosol material for separations carried out from the aqueous phase and carbon for gas chromatographic separations. Transport times of typically two to five seconds were achieved.

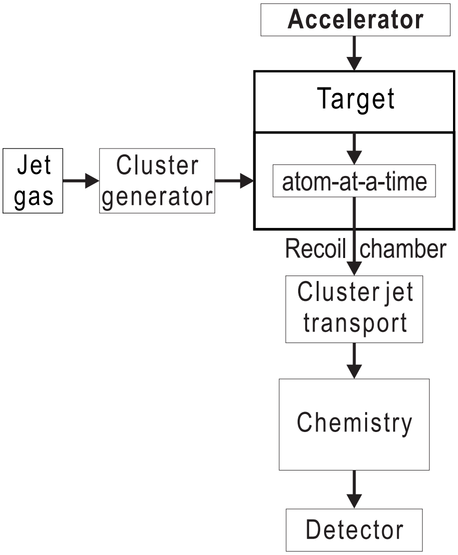

Fig. 3. Schematic presentation of components of recent on-line experiments with the transactinides Rf to Bh.

3.2. Liquid-phase chemistry set-ups

So far, all liquid-phase separations to study the chemical behavior of transactinides were performed in a discontinues, batch-wise operation with large numbers of cyclic repetitions. While in several experiments on Rf and Db manual procedures were used [72], most transactinide separations were carried out with automated instruments as schematically shown in the upper part of Fig. 4. The implementation of the **A**utomated **R**apid **C**hemistry **A**pparatus, **ARCA**, [73] yielded the predominant share of today's knowledge about the chemical behavior of the transactinide elements Rf through Sg in aqueous solution. ARCA II is micro-computer controlled and allows fast, repetitive, and reproducible chromatographic separations in a miniaturized and chemically inert liquid-chromatography system (8 mm long micro-columns of 1.6 mm i.d.) with typical cycle times between 45 s and 90 s. Depending on the chemistry, the columns were filled with cation or anion exchange resin or an organic extractant on an inert support material.

Common to all batch-wise separations are time consuming evaporation steps to prepare one or more samples for α-spectroscopy and to measure spontaneous-fission fragments. Samples are dried by intense IR-light and a stream of hot He-gas. While separation times are normally between 5 s and 10 s, evaporating the aqueous phase requires about 20 s.

A breakthrough concerning the automatization of the sample preparation was achieved with the **A**utomated **I**on Exchange Apparatus Coupled with **D**etection System for **A**lpha Spectroscopy, **AIDA**, [74]. In addition, AIDA includes the automated transport of samples to and from the vacuum chamber for nuclear spectroscopy. AIDA, very similar to ARCA in its part as a chemical separation apparatus — with improvements in some details — has recently been applied to detailed studies of the Rf chemistry [75, 76].

3.3. Gas-phase chemistry set-ups

Continuously operating gas-phase separations [77], like the **O**n-**L**ine **G**as chromatographic **A**pparatus, **OLGA**, [78] were extremely instrumental to study the formation of halide and halide oxide compounds of the transactinides Rf through Bh and to investigate their characteristic retention time — a measure very often expressed as a "volatility". The lower part of Fig. 4 shows a flow scheme of such type of chromatographic separation. Common to all of these experiments is the use of the known nuclide

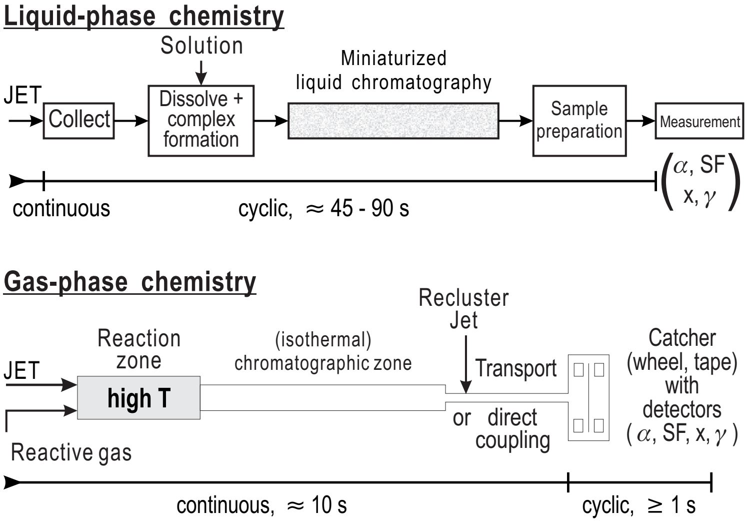

Fig. 4. Schematic flow chart of components for an automated on-line chemistry from liquid phase (upper part) and from gas-phase (lower part).

half-life to determine a "retention-time-equivalent" to gas-chromatographic experiments on an atom-at-a-time scale — its the 50% yield value of a breakthrough curve measured as a function of various isothermal temperatures. The 50%-yield-temperature is equal to the temperature at which, in classical gas-chromatographic separations, the retention time is equal to the half-life of the investigated nuclide. Products leaving the chromatography column are usually attached to new aerosols in a so-called recluster process and are transported in a gas-jet to a detector system like the **RO**tating wheel **M**ultidetector **A**nalyzer, **ROMA**, [79]. Here samples are assayed for time correlated, characteristic α-decays and for spontaneous-fission fragments.

A different experimental approach for gas adsorption studies provides the thermo-chromatography; see *e.g.* [80, 81] and references therein. In this method a (negative) temperature gradient is imposed on the chromatography column and, for the high temperature version of this method, ranging from ≈700 K to ≈300 K, tracks from spontaneous-fission fragments are registered along the chromatography column after the end of the experiment.

More details of gas-phase chemistry experiments are discussed below in the context of the bohrium chemistry. The experimental set-up used their is shown schematically in Subsection 4.4. The very unique experimental technique used for the first chemical identification and investigation of hassium is outlined in Subsection 4.5 together with the experimental results.

4. Experimental results and discussion

Experimental results presented in this section yield important information on the chemical behavior of these elusive elements — for a chemist a value in itself. Assessing these properties in comparison to other elements properties, in view of the structure of the Periodic Table or even to unravel relativistic effects is an increasingly difficult task. Here one should keep in mind that measured quantities — deposition temperatures or retention times in thermo-chromatography or gas-chromatography and elution positions or distribution coefficients in liquid chromatography or in extraction experiments — can straight forward only be compared with the behavior of other elements investigated in the same experiments, and only if all investigated nuclides have about the same half-life. In the interpretation of these results beyond the pure analogy to the lighter homologues, assumptions about, *e.g.*, the oxidation state or the type of compound formed enter. Empirical model assumptions are needed to calculate physico-chemical quantities like adsorption — or sublimation enthalpies. The step towards the interpretation of these results in terms of relativistic effects establishes an even more sophisticated task complicated by other effects in the atoms and molecules like spin-orbit coupling, configuration mixing and shell effects [24].

4.1. Element 104, rutherfordium (Rf)

Already the pioneering experiments of the Rf behavior in the gas phase [33,82] and in acidic, aqueous solutions [34,35] demonstrated that Rf behaves different from trivalent actinides and as expected for a member of group 4 of the Periodic Table with Zr and Hf as their lighter homologues. Many attempts have been made to study the behavior of Rf in comparison with group-4 elements and, in aqueous solution, also with tetravalent Th and Pu ions as pseudo-homologues, see, *e.g.*, Refs [38–41,72,77,83,84] for summaries.

Recent on-line gas chromatographic studies of Rf were carried out in comparison with its lighter group-4 homologues with chlorinating and brominating reagents [85–87]. It was shown in the chloride system [86] that small amounts of oxygen can lead to the formation of a less volatile chloride oxide instead of the pure chloride which may pose a problem to the interpretation of the results. This has serious consequences if there are pronounced differences in the trend how easily Zr, Hf and Rf form a chloride oxide. However, the work of Reference [86] also showed that the formation of pure chlorides can be achieved. Moreover, it was shown that the $RfCl_4$ is more volatile than the $HfCl_4$ [86,88]. This is in agreement with theoretical predictions [89] and is interpreted as a result of relativistic effects. Extrapolations of trends within group 4 yield the opposite trend.

As a large number of new results was obtained in aqueous-phase chemistry experiments of Rf over the last few years only a few exemplary results will briefly be discussed in the following part. These experiments concentrated on the competing strength of hydrolysis and complex formation. To shed more light on this question data were determined with ARCA and, most recently, also with AIDA to study the behavior of Rf in comparison with the lighter homologues Zr and Hf and the pseudo-homologues Th and (tetravalent) Pu.

Differences in the F^--complexation of the group-4 elements Zr, Hf and Rf, and the pseudo-homologue Th were obtained with ARCA in mixed 0.1 M HNO_3/HF solutions on cation exchange resins (CIX) and on anion exchange resins (AIX) [90]. For Zr and Hf K_d values drop on CIX between 10^{-4} M and 10^{-2} M HF. For Rf this decrease is observed at about one order of magnitude higher HF concentration, and it is even higher for Th, *i.e.*, the transition from cationic to neutral and to anionic species requires higher HF concentrations for Rf compared with Zr and Hf but lower concentrations than the ones needed for Th. This establishes the following sequence of F^--complex formation strength at low HF concentrations: $Zr \geq Hf > Rf > Th$.

This result is in agreement with data obtained with AIDA [74] and with theoretical expectations [91]. A complete and quantitative understanding of the Rf behavior requires further quantumchemical calculations and a theoretical treatment of complex formation and hydrolysis of these tetravalent ions.

In the ARCA data on AIX [90], a rise in K_d values from about 10 to more than 100 is observed between 10^{-3} M and 10^{-1} M HF for Zr and Hf measured off-line in batch extraction experiments. This is consistent with the continuation of the trend observed on CIX. For the Th off-line data, and for the Hf and Rf on-line data, no significant rise of the K_d values was observed on AIX between 10^{-3} M HF and concentrations of up to 1 M HF. While this is expected for Th, which does not form fluoride complexes, it comes as surprise for Hf and Rf. How much this is affected by the 0.1 M HNO_3 in solution remains unclear. Presently, these data reflect the best knowledge from these experiments. However, it is obvious that there are still unresolved problems with the consistency between off-line and on-line data. To solve this puzzle, also kinetic effects are presently considered. Therefore, one shall view these AIX data as under discussion.

Earlier experimental results suggest that Rf forms anionic F^- complexes in pure 0.2 M HF [92] and in mixed 0.27 M HF/0.1 M and 0.2 M HNO_3 solutions [93]. It is interesting to note that Rf shows an intermediate behavior between Zr and Hf, with some tendency to be closer to Hf, in the formation of neutral chloride complexes probed with tributylphosphate at 8 M HCl [94].

The formation of anionic chloride complexes of Zr, Hf, and Rf above 8 M HCl was shown in experiments with AIDA [76]. This again clearly indicates the group-4 properties of Rf. A hypothetically Th-like or Pu-like behavior of Rf was probed with an anion exchange resin and 8 M HNO_3. While Th and Pu form anionic complexes which are adsorbed Rf remains in solution [76] as expected for a typical group-4 element with non Th-like and non Pu-like properties.

4.2. Element 105, dubnium (Db)

A normal continuation in the Periodic Table puts element 105, dubnium, Db, (called hahnium, Ha, in many of the early publications) into group 5 below Nb and Ta. Early thermo-chromatographic separations of volatile chloride and bromide compounds showed that Db behaves more like a transactinide than an actinide element [36, 95]. Later investigations with gas-chromatographic methods determined a lower volatility of a Db bromide compound as compared with the lighter homologues Nb and Ta [96, 97].

However, it was also demonstrated for the chloride compounds [77] that group-5 elements have a strong tendency to form a less volatile halide oxide if a small amount of oxygen is present. This may have obscured some of the earlier results. The final comparison on the halide volatility of group 5 elements including Db remains to be performed. This is of importance because of a theoretical result, including relativistic effects, which predicts a higher volatility for $DbBr_5$ as compared with the pentabromides of Nb and Ta [98].

In its first aqueous chemistry Db, was adsorbed onto glass surfaces from HCl and HNO_3 solutions [37], a behavior very characteristic for group-5 elements. An attempt to extract Db fluoride complexes failed under conditions in which Ta extracts but Nb does not [37]. The first detailed comparison between Db, its lighter homologues Nb and Ta, and the pseudo-homologue Pa was carried out from solutions at different HCl concentrations with small amounts of HF added. They were performed as liquid-liquid extraction chromatography experiments with triisooctyl amine, TIOA, as a stationary phase on an inert support in ARCA. In these experiments Db showed a striking non Ta-like behavior. At 0.5 M HCl/ 0.01 M HF, Db even showed Pa-like properties [99, 100].

The interpretation of these results is hampered by the use of the mixed HCl/HF solution that did not allow clearly distinguishing which complex was formed. In contrast to the experimentally observed extraction sequence from HCl solutions with small amounts of HF added, the inverse order $\mathrm{Pa} \gg \mathrm{Nb} \geq \mathrm{Db} > \mathrm{Ta}$ was theoretically predicted [101] for the extraction from pure HCl solutions. This work considered the competition between hydrolysis [102] and chloride complex formation. Recent experimental studies performed in the pure F^-, Cl^-, and Br^- system [103] are in excellent agreement with the theoretical predictions which include relativistic effects [101, 104]. The fluoride complexation of Db in 0.2 M HF was most recently confirmed in an experiment with the set-up **RACHEL** [105] which contains three consecutive ion-exchange columns — a CIX column, an AIX column and another CIX column. It was shown that an anionic fluoride complex of Db is strongly retained on the anion exchange resin.

For the system Aliquat 336(Cl^-) and (pure) 6 M HCl an extraction sequence of $\mathrm{Pa} > \mathrm{Nb} \geq \mathrm{Db} > \mathrm{Ta}$ was determined, see Fig. 5, which — in agreement with theoretical predictions [101, 104] — is inverse to that in HCl solution containing some HF. K_d-values of 1440, 683, 438^{+532}_{-166}, and 22 were measured for the Pa, Nb, Db and Ta, respectively, in series of off-line and on-line experiments. More information on other, previously performed experiments is given in [38, 39, 41, 72].

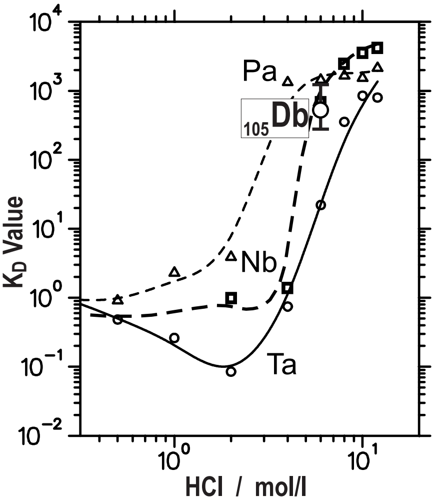

Fig. 5. Coefficients for the extraction of Ta (small circles, solid line), Nb (squares, long-dashed line), and Pa (triangles, short-dashed line) tracers from pure HCl solutions at various concentrations into Aliquat 336(Cl$^-$). The K_d of Db at 6 M HCl (large circle) is plotted with error bars encompassing 68% confidence limits. Data from [103].

4.3. Element 106, seaborgium (Sg)

The first chemical separations of element 106, seaborgium, Sg, to probe its behavior in comparison with its lighter group-6 homologues Nb Mo and W in an aqueous solution were performed from 0.1 M HNO_3/ 5×10^{-4} M HF on a cation exchange resin in ARCA [69,106]. Seaborgium, detected through three correlated α-decays of the Rf- and No-daughter nuclei, elutes together with the hexavalent ions of Mo and W; see Fig. 6 for a chromatogram from W-tracer studies. Hexavalent U-ions, present as UO_2^{2+} cations, are strongly retained on the column as divalent, trivalent and tetravalent ions are. This result shows that the most stable oxidation state of Sg in aqueous solution is +6, and that, like its homologues Mo and W, Sg forms neutral or anionic oxide or halide oxide compounds. Under the given condition, Sg exhibits properties very characteristic of group-6 elements, and does not show U-like properties.

A second experiment was performed with pure 0.1 M HNO_3 to probe the influence of the F$^-$ anions on the complex formation [107]. Contrary to the lighter homologues elements Mo and W, seaborgium was not eluted from the CIX in pure 0.1 M HNO_3. From this it can be concluded that F$^-$ anions significantly contributed to the complex formation in the first experi-

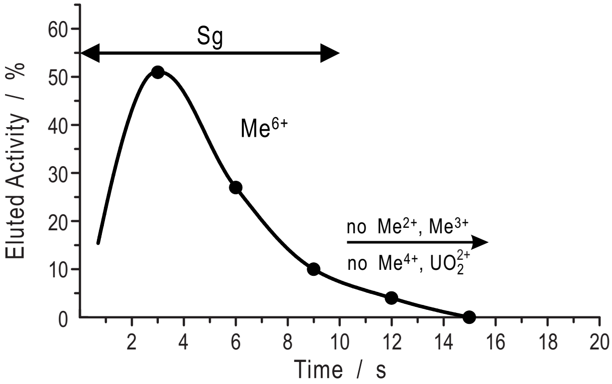

Fig. 6. Elution curve for W-tracer (Me^{6+}), modeling the Sg separation on ARCA in 0.1 M $HNO_3/5\times10^{-4}$ M HF, together with "lower limit" (lower right arrow) for the elution of di- , tri-, tetravalent ions, and UO_2^{2+}. Elutions were performed at room temperature with a flow rate of 1 ml/min from 1.6×8 mm columns filled with the 17.5±2 μm particle size cation exchange resin Aminex A6. From [106].

ment. This rules out that Sg was eluted as $[SgO_4]^{2-}$ in the first experiment while the formation of the neutral compound SgO_2F_2 or the anionic complex $[SgO_2F_3]^-$ seems to be likely. The non-tungsten like behavior of Sg in pure HNO_3 may be attributed to its weaker tendency to hydrolyse [107, 108]. While Mo and W can reach the neutral species $MO_2(OH)_2$ (M=Mo, W) for Sg hydrolysis presumably stops at $[Sg(OH)_5(H_2O)]^+$ (sometimes characterized as $[SgO(OH)_3]^+$) [108] or already even at $[Sg(OH)_4(H_2O)_2]^{2+}$.

Studies of the formation and of the volatility of halide oxide compounds [109] and of hydroxide oxide compounds [110] of Sg were performed in gas-adsorption chromatographic experiments. Break-through curves were measured in the gas-chromatographic experiments [69, 109] in the temperature range between about 420 K and 670 K in fused silica columns with the set-up OLGA for Mo, W and Sg compounds in an oxygen containing strong chlorinating atmosphere (Cl_2 saturated with $SOCl_2$ and traces of O_2). Under these conditions, the formation of MO_2Cl_2 compounds (M = Mo, W, Sg) is most likely . The sequence in volatility of $MoO_2Cl_2 > WO_2Cl_2 \approx SgO_2Cl_2$ was established and adsorption enthalpies of $-\Delta H_a(MoO_2Cl_2)=90\pm3$ kJ mol^{-1}, $-\Delta H_a(WO_2Cl_2) = 96\pm1$ kJ mol^{-1} and $-\Delta H_a(SgO_2Cl_2) = 98^{+2}_{-5}3$ kJ mol^{-1} were deduced. This Sg behavior is in line with extrapolations in group 6 of the Periodic Table. A detailed discussion of the thermochemical characterization of Sg is given in Ref. [111].

Qualitatively similar experimental results were obtained applying a thermo-chromatographyic technique [88,112]. The authors of this study discussed, in addition to the formation of a group-6 dichloride dioxide, a more volatile species, like the $WOCl_4$. This may be formed slowly and, therefore, may only be of relevance for the observation of long-lived W isotopes which can migrate to a lower column temperature.

Group-6 element hydroxide oxide compounds were studied with high temperature gas-chromatography apparatus **HITGAS** at about 1300 K [110]. O_2 gas, saturated with H_2O at 323 K, was added as a reactive gas to the He carrier. From the observation of Sg compounds passing through the column it was concluded that Sg forms a volatile hydroxide oxide, a property typical for group-6 elements.

4.4. Element 107, bohrium (Bh)

So far, the only information on the chemical properties of bohrium was obtained in gas chromatographic experiments [64] with an experimental set-up schematically shown in Fig. 7. The investigation of volatile Me(VII) halides oxides was an obvious way to study Bh in comparison with the lighter group-7 homologues elements Tc and Re according to their intermediate position between the lighter transactinides, which form volatile halides, and the highly volatile group-8 tetroxides.

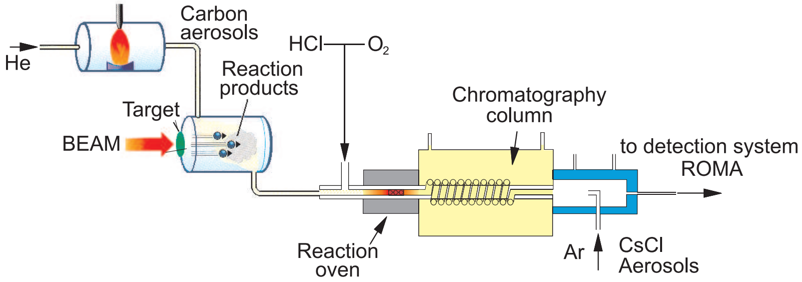

Fig. 7. Schematic view of the Bh gas-chromatography experiment. Adapted from [64].

Nuclear reaction products were carried with C-aerosols as a cluster material from the recoil chamber to the OLGA. The reactive gases HCl and O_2 were added in front of the high temperature zone of the reaction oven where C-aerosols were burned and where the compounds MeO_3Cl (Me=Tc,Re,Bh) were formed. Relative yields of the compounds which are breaking through were measured as a function of the isothermal temperature in the quartz chromatography column. CsCl was used as a re-cluster material in the Bh experiments to transport those compounds which leave the chromatography column to the detection system ROMA.

From the observation of four ^{267}Bh nuclear-decay chains at 453 K (isothermal chromatography temperature), two at 423 K, and zero at 348 K a

BhO_3Cl break-through curve was modelled, based on the Monte Carlo Method outlined in Ref. [113], and was compared with known curves from tracer studies with lighter homologues elements [64]. The characteristic 50% yield of the BhO_3Cl curve is located at a higher temperature compared with the ReO_3Cl and the TcO_3Cl behavior.

Qualitatively, this results shows that Bh behaves like a member of group 7 of the PTE and that it forms a volatile halide oxide — presumably BhO_3Cl as inferred from its properties — which is less volatile than the compound of the lighter homologues elements [64]. More quantitatively, the deduced BhO_3Cl adsorption enthalpy is in good agreement with a theoretical prediction including relativistic effects [114]. This result coincides with the value expected from empirical correlations of thermochemical properties and with Bh positioned in group 7 of the Periodic Table [64].

4.5. Element 108, hassium (Hs)

Very recently, the first chemical separation and identification of a Hs compound was achieved [61, 62]. From its expected chemical properties as a member of group 8 of the Periodic Table it is most attractive to investigate the highly volatile tetroxide — a unique property only known for group 8 transition metals. The experiment was performed at the UNILAC accelerator at GSI with a set-up schematically shown in Fig. 8. This experiment was unique, in a number of aspects, and different from recent gas-chromatographic experiments:

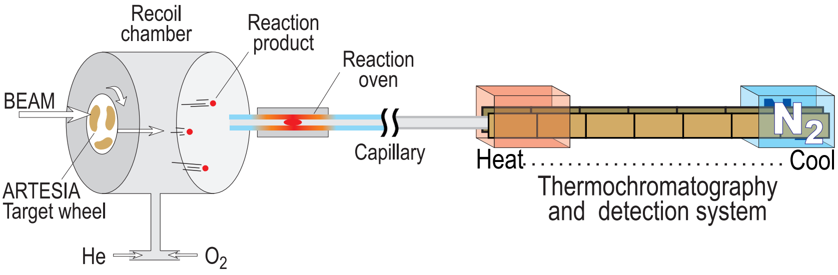

Fig. 8. Schematic view of the low temperature thermo-chromatography experiment to investigate HsO_4. Adapted from [61].

(i) A rotating target wheel ("ARTESIA" in Fig. 8) for ^{248}Cm targets in combination with a gas-jet transport system was applied for the first time in transactinide chemistry to accept higher beam intensities.

- *(ii)* The chemical reaction with the reactive gas O_2 was performed "in-situ" in the recoil chamber **IVO**, **I**n situ **V**olatilization and **O**n-line **D**etection [61,115]. An oven attached to the recoil chamber provided a fast and efficient oxidation of the stopped recoils. This allowed transporting highly volatile compounds without any cluster material in a dry He/O_2 gas mixture over 10 m in a Teflon capillary to the detection system. It should be noted that already earlier work, *e.g.* some studies on the halide volatility of Rf and on Sg, used a chemical reaction in or immediately behind the recoil chamber directly attached to a thermo-chromatography column, see [81, 83] and references therein.
- *(iii)* An on-line thermo-chromatography separator and detector set-up, **COLD**, **C**ryo **O**n-line **D**etector [61], operated at low temperatures was mainly used. This is an improved version of the previously developed **C**ryo-**T**hermochromatography **S**eparator, **CTS**, [116], which was also used during this beam time. COLD consists of 12 pairs of three silicon PIN-photodiodes each (with silicon nitride surfaces) coupled to a support which provides the negative temperature gradient between about 250 K at the entrance side and about 100 K at the gas exit.

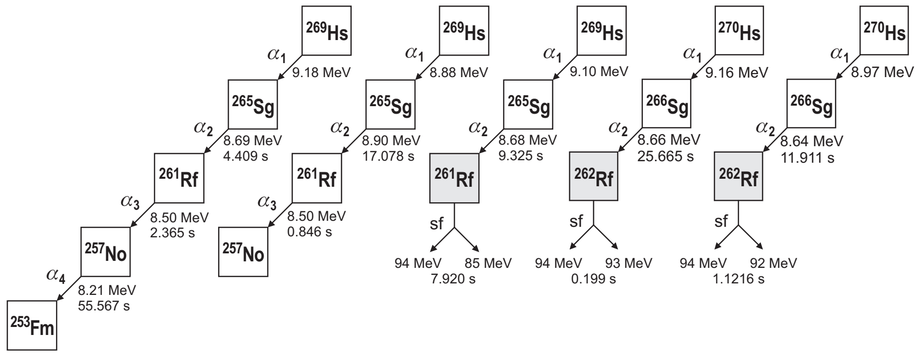

Fig. 9. Nuclear decays chains from Hs isotopes observed in the first chemistry experiment of element 108. Indicated are the registered energies for α-particles and fission fragments and the lifetimes. Adapted from [61,62].

Nuclear decay chains originating from the known isotope ^{269}Hs and from the isotope ^{270}Hs, for which first evidence was obtained in the course of this experiment, were observed [62] in a narrow peak [61] along the temperature gradient; see Fig. 9 for the observed nuclear decay chains and Fig. 10 for their distribution along the temperature gradient. From the observation of HsO_4 and its adsorption position at 229±6 K, in comparison with the known one of OsO_4 at 191±7 K, one concludes that Hs forms a relatively

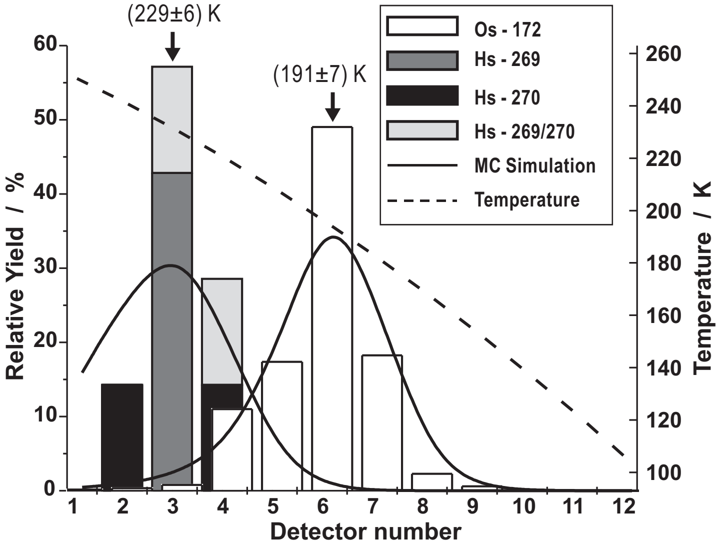

Fig. 10. Experimentally observed thermo-chromatogram of HsO_4 (full histogram peaked at detector 3) and of OsO_4 (open histogram peaked at detector 6) given in relative yields. Solid lines represent results of a Monte Carlo Simulation of the migration process of $^{269}HsO_4$ and $^{172}OsO_4$ along the temperature gradient assuming standard adsorption enthalpies of -46.0 kJ mol^{-1} and -39.0 kJ mol^{-1}, respectively. The dashed line indicates the temperature profile (right-hand scale). Adapted from [61].

stable, volatile tetroxide — as expected for a typical member of group 8 [91, 117]. However, the exact adsorption position is at a surprisingly high temperature [61], *i.e.*, HsO_4 exhibits an unexpected low volatility or, in other terms, a high, negative adsorption enthalpy. As enthalpies of adsorption on silicon nitride, evaluated from the measured deposition distributions, values of $-\Delta H_{\mathrm{a}}^{\circ(T)}(HsO_4)=(46\pm2)$ kJ/mol for HsO_4 and $-\Delta H_{\mathrm{a}}^{\circ(T)}(OsO_4)=(39\pm1)$ kJ/mol for OsO_4 were deduced from a fit of a Monte Carlo simulation (solid line Fig. 10) to the experimental data [61].

5. Summary

As has already been observed in earlier experiments, the results from these more recent studies again justify positioning of the transactinides — or superheavy elements — beginning with element 104, into the seventh period of the Periodic Table, see Fig. 1. So far chemical studies on their behavior have been performed with Rf, Db and Sg in the aqueous phase. Studies in the gas phase — also performed for Rf, Db and Sg — have recently been extended to Bh and have now reached Hs. All experimental results yield properties which place these elements into their respective group of the Periodic Table — Rf, Db, Sg, Bh, Hs into group 4, 5, 6, 7, and 8, respectively. This demonstrates that the Periodic Table still remains an appropriate ordering scheme.

However, a closer and more subtle look reveals that all the more detailed chemical properties of these elements — in comparison with their lighter homologues — are no longer reliably predictable by simple extrapolations in the Periodic Table. But modern relativistic molecular calculations in combination with empirical models allow for quantitative, or semi-quantitative, comparisons of experimental and theoretical results, and they show excellent agreement in a number of cases. From this one can deduce that relativistic effects strongly influence the chemical properties of the transactinides and comparisons with results from theoretical model calculations can give indications what facets of the chemical properties are predominately due to relativistic effects. This is expected to become much more distinct when proceeding to even heavier elements.

6. Perspectives

Fascinating and challenging prospects are ahead to explore the recently "chemically discovered" region between element 106 and element 108. Even more interesting and more challenging will be the future attempts to extend the chemical separation and characterization of superheavy elements all the way to element 114 — and, sometime maybe even beyond. Recent results from the reaction of ^{48}Ca ions with ^{238}U and ^{242,244}Pu targets [27, 29, 30] indicate the existence of relatively long-lived nuclides of elements 108 to 114 between neutron number N=169 and N=174. Their half-lives are ideal for chemical studies. However, as cross sections are painfully low, this situation primarily calls for an increase of production rates through higher heavy-ion beam intensities and developments of new target designs which can tolerate these intensities.

Prospects to study chemical properties of superheavy elements beyond element 106 in the aqueous phase mainly depend on the development of methods to cope with production rates of less than one atom per hour. Two types of continuously operating liquid-chemical separation processes are presently emerging for superheavy elements. The one with a truly continuous separation and detection technique is the fast, automated and miniaturized centrifuge system **SISAK** [118–121] which allows separating nuclides with half-lives of the order of 1 s. Separations are based on liquid-liquid extractions with subsequent phase separation and detection of the α-decay and spontaneous fission in the organic phase with an extractive liquid scintillator [122].

A different approach to continuously separate transactinide elements and to establish their chemical behavior from the observation of long-lived daughter isotopes in one or another chemical fraction was introduced with the three- or multi-column technique [92, 93, 105, 123]. Because of its continuous operation, this technique may allow extending these studies to nuclides with cross sections below the nanobarn level. Preparations are under way to perform such studies to determine differences in the hydrolysis and complex formation of Mo, W, and Sg [124] and to investigate group 7 and group 8 elements in aqueous solution [125]. Existing separation techniques, like ARCA and AIDA, will remain essential tools to shed more light on the diverse and often unexpected behavior of the lightest superheavy elements.

Well developed gas-phase chemistry techniques are at hand to deepen our insights into many unresolved questions of compound formation, volatility and adsorption behavior of group 4 through 8 halides, oxides and mixed compounds. A challenge for the future will be the gas-phase studies of the metallic transactinides beyond group 8. Element 112 has a very unique position in this row with Hg as its lighter homologue in group 12. Here the future has already begun with first attempts to distinguish between a Hg-like and a much more inert Rn-like behavior of element 112 in a gas adsorption experiment with reactive Au surfaces [126].

Coupling of chemical separation set-ups to physical recoil separators will provide a big leap into a completely new quality of separation and detection of superheavy elements. A first and successful step into this direction was made by coupling the SISAK system to the **B**erkeley **G**as-filled **S**eparator (**BGS**) for a Rf chemistry [121]. Gas-chromatographic techniques and the emerging vacuum thermo-chromatography techniques [127] are almost ideally suited for such coupling schemes.

In addition to fascinating chemistry aspects, these experiments provide multifaceted nuclear data and they are vital tools for a clear identification of the atomic number of relatively long-lived spontaneously-fissioning nuclides at the end of α-decay chains on the pb level.

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