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Chemistry of superheavy elements

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Summary. The chemistry of superheavy elements – or transactinides from their position in the Periodic Table – is summarized. After giving an overview over historical developments, nuclear aspects about synthesis of neutron-rich isotopes of these elements, produced in hot-fusion reactions, and their nuclear decay properties are briefly mentioned. Specific requirements to cope with the one-atom-at-a-time situation in automated chemical separations and recent developments in aqueous-phase and gas-phase chemistry are presented. Exciting, current developments, first applications, and future prospects of chemical separations behind physical recoil separators ("pre-separator") are discussed in detail. The status of our current knowledge about the chemistry of rutherfordium (Rf, element 104), dubnium (Db, element 105), seaborgium (Sg, element 106), bohrium (Bh, element 107), hassium (Hs, element 108), copernicium (Cn, element 112), and element 114 is discussed from an experimental point of view. Recent results are emphasized and compared with empirical extrapolations and with fully-relativistic theoretical calculations, especially also under the aspect of the architecture of the Periodic Table.

1. Introduction and historical remarks

Half a century ago, in the year 1962 – at the time when Radiochimica Acta was launched – the last element of the actinide series [1], element 103, was just making its way into the Periodic Table of the Elements (PTE), see Fig. 1. It was one year earlier, when the article "New Element, Lawrencium, Atomic Number 103" [2] had appeared. The heated atmosphere of the cold war – cumulating in the Cuban Missile Crisis in 1962 –, also casted dark shadows on the scientific competition between groups in the two blocks. Reference [2] provided strong evidence for the synthesis of element 103 but it was only the opening for a decade long race to pin down its existence and to determine first properties in physical and chemical experiments at both Berkeley and Dubna. Finally, 30 years later, the Transfermium Working Group (TWG) of the International Union of Pure and Applied Chemistry (IUPAC) and its counterpart in physics (IUPAP) suggested that credit for the discovery should be shared by the two laboratories and accepted the name lawrencium [3]. An important lesson learned in the evaluation of discovery claims of the heaviest actinides and first transactinides was summarized by the TWG in noticing that the "discovery" of an element (i) "is not always a single, simply identifiable event or even culmination of a series of researches but may rather be the product of several series of investigations" and (ii) that the judgment of what is sufficient evidence to convince the scientific community that the formation of a new element has, indeed, been established, may vary from group to group [3].

Already in the year 1961, after the new heavy ion cyclotron U300 went into operation at Dubna, a search for the first transactinide element with atomic number 104 had begun. In 1962, it resulted in an unexpected and exciting "by-product": the discovery of spontaneously fissioning isomers by Polikanov *et al.* [4]. In heavy element science, the 1960s were a time of important developments – often technical ones not only influencing and advancing experimental capabilities but also having great impact on new developments in nuclear theory. Those were closely connected to the use of the newly arriving computer. It was one key event, the conference at Lysekil in the year 1966 [5], which gave the starting signal for the rush into the new era of superheavy element science. In this year, seminal work by Myers and Swiatecki [6] and by Sobiczewski and coworkers [7] was published, and Meldner [8] presented his outstanding work at Lysekil. While early and more qualitative work of Wheeler [9] – who coined the term superheavy element – and Scharff-Goldhaber [10] made it conceivable that superheavy elements may exist around atomic number $Z = 126$, these new results now focused on the existence of an "island of stability" centered at $Z = 114$ and neutron number $N = 184$. As first estimates yielded relatively long half-lives as long as a billion years, immediately a gold-rush period of hunting for superheavy elements (SHE) started, at first in nature – in terrestrial and extra-terrestrial samples - and later at accelerators. Reviews concentrating on various aspects of the experimental work of this early phase can be found in [11–19]. An overview over the first century of nuclear and radiochemistry is given in [20].

Over the last 50 years, discoveries of 15 new chemical elements with a total of about 100 new nuclides have been claimed – all of them transactinides. Today's Periodic Table of the Elements shows 118 chemical elements of which

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112 are accepted and named by the IUPAC; for elements 114 and 116 see Sect. 5.8. The most recent one was element 112, copernicium, Cn, [21, 22]. The isotope ^{277}112 was discovered by Hofmann and coworkers at the GSI [23, 24] in a "cold fusion" reaction (see Sect. 2.2) leading to rather neutron-deficient nuclei of transactinide elements. These nuclei are, because of their very short half-life, of very limited use for chemical studies [25]. Certainly, cold fusion reactions provided a very successful road synthesizing elements 107 to 112 at GSI's recoil separator SHIP; for reviews see [26, 27]. However, the synthesis and proof of existence of element 113 in the ^{70}Zn on ^{209}Bi reaction [28, 29], an experiment carried out by Morita and coworkers over many years at the GAs-filled Recoil Ion Separator (GARIS) at RIKEN's Nishina Center, has shown to be extraordinary difficult. Element 113 possibly marks the end of the cold fusion path into the heaviest elements.

It was at the Flerov Laboratory of Nuclear Reactions (FLNR) in Dubna where, over the last decade, Oganessian and coworkers carried out large series of experiments irradiating targets ranging from ^{238}U to ^{249}Cf with ^{48}Ca beams. Products were separated with the Dubna Gas-Filled Recoil Separator (DGFRS). These experiments provided a breakthrough and led to the (only for elements 114 and 116 officially accepted) discovery of elements up to 118 [30, 31]; an overview is given in [32, 33]. Results from a ^{48}Ca on ^{238}U experiment at SHIP [34] support data about the synthesis and decay of 3.8-s ^{283}Cn [35]. The synthesis of the most neutron-deficient know isotope of element 114, ^{285}114 ($T_{1/2} \approx 0.1$ s) [36], was achieved in an experiment at the Berkeley Gas-filled Separator (BGS). Recently, exciting news came from an experiment at GSI's gas-filled separator named TransActinide Separator and Chemistry Apparatus (TASCA). It confirmed the synthesis of the two most neutron-rich isotopes of element 114, 0.69-s ^{288}114 and 2.1-s ^{289}114 [37]. Moreover, it showed that these two isotopes are produced with a cross section of the order of 10 pb [38] – the highest cross section observed in ^{48}Ca induced production of transactinides. These nuclei have longer half-lives and are produced with much higher cross sections than the ones in cold fusion reactions, thus providing great perspectives for chemical studies. In contrast to the discovery of elements 107 to 112, these experiments suffer a disadvantage that their nuclear decay is not "genetically" linked by unequivocal α-α-decay sequences to the region of known nuclei – a prerequisite for unique identifications. A review on production and properties of transactinides can be found in [39].

Chemistry – in addition to unraveling exciting chemical properties – may become a crucial tool in elemental identification. To that end chemical experiments have to demonstrate unique chemical properties of a new element under investigation – possibly together with characteristic nuclear decay properties – excluding any other chemical element. A step into this direction was made by the first successful gas-phase chemistry experiment with Cn [40, 41]. It provided the first independent confirmation of reports about syntheses of elements 112 and 114. More details are discussed in Sect. 5 together with chemical properties of Cn.

Now, we turn our view to chemistry. 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) – and, from a chemical point of view, they are transactinide elements. In agreement with Seaborg's empirical actinide concept [1], analog to the sixth period of the PTE, a new series of 6*d*-transition elements begins with element 104 followed by 7*p* elements from atomic number 113 to 118 [42, 43]. Important and interesting questions for chemists concern the position of superheavy elements in the PTE and related chemical properties - especially in comparison with their lighter homologs in the respective groups; see Fig. 1. Chemical properties similar to those known from lighter transition metals in the fifth and sixth period can be anticipated. However, it is by no means trivial to assume that transactinides will exhibit chemical properties, which can in detail easily be deduced from their position. To which extent the PTE is still a valid ordering scheme regarding chemical properties is a key question.

Relativistic atomic and molecular calculations clearly show a large influence of direct and indirect relativistic effects on the energetic position and the sequence of electrons in their respective orbitals. This is associated with changes in their radial distributions. All of these relativistic changes are so pronounced that, if compared with non-relativistic calculations, significantly different chemical properties than anticipated for SHE would not be surprising. Thus, 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. Reviews of recent theoretical work including predictions of chemical properties can be found in [44–49]. Ground-state electronic configurations and information on oxidation states are listed in Table 1.

First generation experiments with Rf [50–52] and element 105, dubnium, Db, [53] rendered enough justification to place Rf into group 4 and Db into group 5 of the PTE. Chemical properties of SHE, or transactinide elements, have been

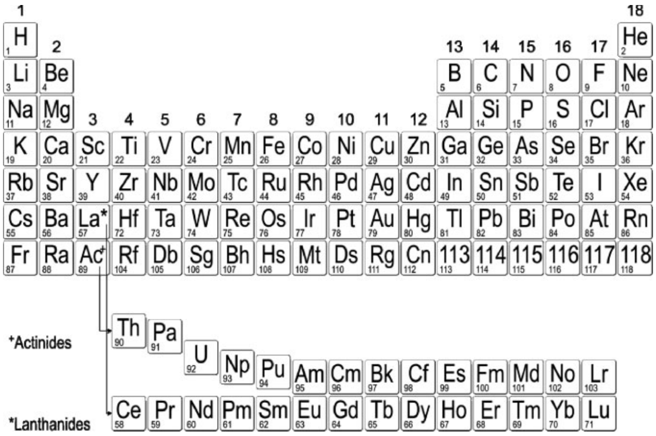

Fig. 1. Periodic Table of the Elements. The IUPAC accepted and named transactinide or superheavy elements 104–112 take the positions of the seventh-period transition metals below Hf in Group 4 and Hg in Group 12; see Sect. 5.8 for the names proposed for elements 114 and 116. Experimental evidence on the synthesis of elements 113 to 118 is convincing enough to also place these elements into the Periodic Table.

Table 1. Ground-state electronic configuration and stable oxidation states for SHE. Table from [25] with data from [47, 48].

Element	Group	Electronic configuration (core: [Rn]$5f^{14}$)	Stable oxidation state^a
104, Rf	4	$6d^2\,7s^2$	3, $\underline{\boldsymbol{4}}$
105, Db	5	$6d^3\,7s^2$	3, 4, $\underline{\boldsymbol{5}}$
106, Sg	6	$6d^4\,7s^2$	4, $\underline{\boldsymbol{6}}$
107, Bh	7	$6d^5\,7s^2$	$\underline{3}$, 4, 5, ***7***
108, Hs	8	$6d^6\,7s^2$	$\underline{3}$, $\underline{4}$, 6, ***8***
109, Mt	9	$6d^7\,7s^2$	$\underline{1}$, 3, 6
110, Ds	10	$6d^8\,7s^2$	0, 2, 4, 6
111, Rg	11	$6d^9\,7s^2$	−1, **3**, **5**
112, Cn	12	$6d^{10}\,7s^2$	***0***, 2, **4**
113	13	$6d^{10}\,7s^2\,7p$	**1**, 3
114	14	$6d^{10}\,7s^2\,7p^2$	0, **2**, 4
115	15	$6d^{10}\,7s^2\,7p^3$	**1**, 3
116	16	$6d^{10}\,7s^2\,7p^4$	**2**, 4
117	17	$6d^{10}\,7s^2\,7p^5$	−1, 1, **3**, 5
118	18	$6d^{10}\,7s^2\,7p^6$	**2**, **4**, 6

a: Bold = most stable oxidation state in the gas phase. Underlined = most stable in aqueous solution. Italics = experimentally observed oxidation states.

studied up to element 108 and first experiments on element 112 and 114 have been performed.

This article briefly deals, in its first part, with nuclear aspects related to the synthesis and nuclear decay of superheavy elements – including a definition of SHE. It will be shown that only single, short-lived atoms are available for chemical studies. This section is followed by a short discussion of theoretical work. The central part presents selected experimental results and techniques applied to determine chemical properties of elements 104 to 106, seaborgium, Sg, in the liquid phase and up to elements 107, bohrium, Bh, and 108, hassium, Hs, in the gas phase. Recent experiments on elements 112 and 114 will be discussed together with new developments und perspectives. The role of physical recoil separators will be outlined. Reviews on the experimental results of SHE chemistry experiments can be found in [25, 54–61] and the comprehensive work of [62].

2. Nuclear aspects

2.1 The region of superheavy elements

Until the early 1980s it was believed that a remote nuclear “island of stability” would exist around $Z = 114$ and $N = 184$ which is surrounded by a “sea of instability” [63, 64]. Up to that time, and typical for closed-shell nuclei, SHE were expected to have a *spherical* shape. However, in 1984 the discovery of element 108 [65] led to a different opinion. New experimental results [66–68] and theoretical concepts, which take into account shell-stabilized *deformed* nuclei and emphasize the importance of the $N = 162$ neutron shell [69–71], show that there is no “island of stability” in a “sea of instability”. Instead, there is a region of shell-stabilized, *deformed* superheavy nuclei with enhanced stability against spontaneous fission (SF) centered at the doubly-magic nucleus ${}^{270}_{108}\mathrm{Hs}_{162}$ [72]. These deformed nuclei connect the world of known nuclei with the still to be explored region of spherical SHE with its unknown location of maximum shell stability – the big challenge in SHE research. Theoretical results indicate that nuclei with atomic number 120 [73, 74] and 126 [75] are good candidates for the next closed shell; with a possibility of an even more pronounced shell stabilization than in element 114.

In the following, an argument is developed to show that it is justified to begin the superheavy elements with element 104 [25, 76]. The result is especially appealing in as much as the beginning of superheavy elements coincides with the beginning of the transactinide elements. Two definitions or assumptions are used. Firstly, superheavy element is a synonym for an element which only exist because of the stabilization through nuclear shell effects. Secondly, only those composite nuclear systems that live at least 10^{-14} s shall be considered a chemical element. This time is well justified from chemical aspects, *e.g.*, from the minimum formation time of a molecule like hydrogen. Now we apply these two assumptions to a comparison of calculated and experimentally observed SF half-lives – the most drastic, spontaneous disintegration of a heavy nucleus. If no extra shell stabilization is in effect, theoretically calculated half-lives fall below the 10^{-14} s mark for elements 104 and higher [25, 39, 76]. The experimentally observed, up to factors of 10^{17} longer half-lives for isotopes of element 104 show the influence of the shell stabilization. From this, one can claim that all elements beginning with element 104 live only because of their microscopic shell stabilization and, therefore, shall be called superheavy elements.

2.2 Nuclear syntheses and decays

While transuranium elements up to and including fermium ($Z = 100$) can be produced by stepwise neutron capture followed by β^--decay, transfermium elements can only be man-made by nuclear reactions with heavy ions at accelerators. In these reactions, one has to overcome the Coulomb barrier between the two positively charged, approaching atomic nuclei. Therefore, the combined, fused system, which is called the compound nucleus, carries a certain amount of excitation energy. The availability of suitable ion beams and target materials – and the energy balances associated with these combinations – allow a crude distinction between two types of reactions: One is termed “cold fusion” and the other one “hot fusion”.

Cold-fusion reactions are characterized by relatively low excitation energies of about 10–15 MeV. They occur when medium-heavy projectiles, *e.g.*, ^{58}Fe, fuse (at the lowest possible energy) with ^{208}Pb or ^{209}Bi target nuclei. There are many advantages with these reactions which, among others, helped to discover elements 107 through 112 [26, 27]. However, a severe disadvantage for chemical studies are very short half-lives of the relatively neutron-deficient nuclei produced. With one exception [77] cold-fusion reactions are usually not used in chemical studies of the heaviest elements.

Hot-fusion reactions are characterized by excitation energies of 35 MeV to 55 MeV when nuclei from ^{238}U to ^{249}Cf fuse with beams from ^{18}O to ^{48}Ca. Consequently, three to five neutrons are emitted before the compound nucleus has cooled. Still, because of the neutron-richness of actinides targets, these reactions yield the more neutron-rich, rela-

Table 2. Nuclides from hot fusion reactions used in SHE chemistry.

Nuclide	$T_{1/2}$/s	Target	Beam	σ
^{261}Rf	78	^{248}Cm	^{18}O	10 nb
^{262}Db	34	^{249}Bk	^{18}O	6 nb
$^{265a+b}$Sg	9 + 16	^{248}Cm	^{22}Ne	380 pb
^{267}Bh	17	^{249}Bk	^{22}Ne	$\approx$ 70 pb
^{269}Hs	9.7	^{248}Cm	^{26}Mg	7 pb
^{283}Cn ^{a}	3.8	^{238}U	^{48}Ca	$\approx$ 2 pb
^{287}114	0.48	^{242}Pu	^{48}Ca	3.5 pb
$\to \alpha +$				
^{283}Cn	3.8			
^{288}114	0.69	^{244}Pu	^{48}Ca	10 pb
^{289}114	2.1	^{244}Pu	^{48}Ca	8 pb

a: So far, directly produced ^{283}Cn was not unambiguosly identified after chemical separation.

tively long-lived isotopes used in chemical investigations of SHE; see Table 2 for used nuclides and [25, 32, 37, 38, 60, 78, 79] for more details.

Cross sections for the syntheses of neutron-rich transactinides in hot fusion reactions vary from about ten nanobarn to a few pb. With typical beam intensities of 3×10^{12} heavy-ions per second and targets of about 0.8 mg/cm^2 thickness ($\approx 2 \times 10^{18}$ atoms/cm^2), production yields range from a few atoms per minute for Rf and Db isotopes to eight atoms per hour for ^{265}Sg, less than two atoms per hour for ^{267}Bh, and a few atoms per day for ^{269}Hs and element 114 isotopes. As half-lives are too short to accumulate many atoms produced at such rates, all chemical separations are performed with single atoms on an atom-at-a-time scale [25, 60].

Alpha decay, the most prominent decay mode for these nuclides, see Fig. 2, provides a unique nuclide identification of investigated products. In the absence of high background count rates, time-correlated subsequent mother-daughter α-α-decay chains provide unambiguous signals. They are used to identify these nuclides in specific chemical fractions or at characteristic positions after chemical separation. Observing α-particles or SF fragments is the only means of detecting individual atoms after chemical separation. It can be performed with a very high efficiency. In addition, new nuclear decay properties were obtained in the course of chemistry experiments as a "by-product" and chemistry was used as a highly efficient Z-separator (Z = atomic number) for nuclear studies. These experiments not only yielded new isotopes like ^{271}Hs [80], but were also instrumental in confirming the observation of new elements [41, 81].

3. Objectives of studies on superheavy element chemistry

3.1 Architecture of the Periodic Table

The Periodic Table of the Elements, see Fig. 1, is the basic ordering scheme for chemical elements and an important tool in predicting their chemical behavior. Conceptually, it

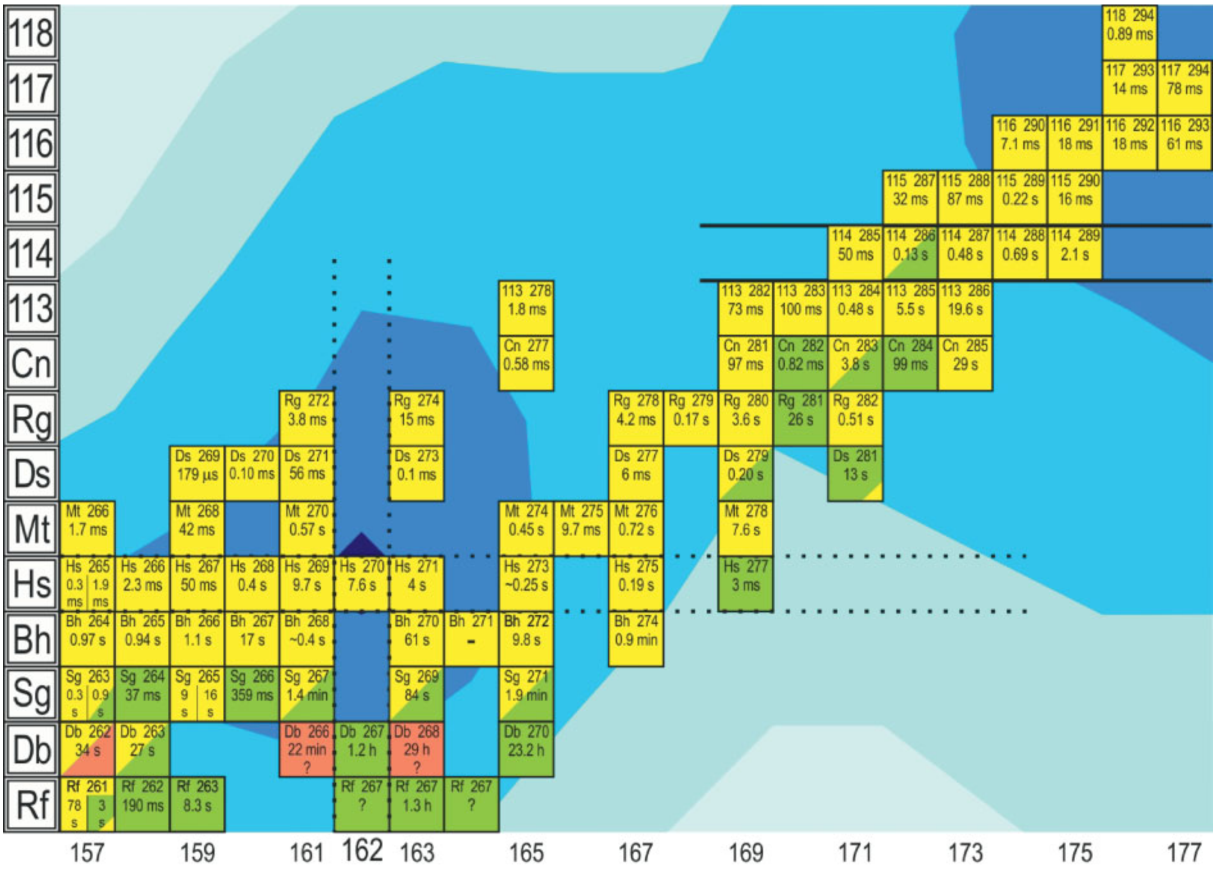

Fig. 2. Upper part of the chart of nuclides showing SHE nuclides with mass number $A > 260$. Regions of enhanced nuclear stability around $Z = 108$ and $N = 162$ (dashed lines) for deformed nuclei and around $Z = 114$ (solid line), $N = 184$ (outside the drawn area) for spherical nuclei are indicated in dark blue. Adapted from [25] and updated.

is, at first, the atomic number and the associated electronic configuration of an element that define its position in the PTE. Secondly, related to this position are chemical properties that arise from the electronic configuration. Trends in chemical properties can be linked to trends in electronic configurations along groups or periods. However, simple extrapolations must be used cautiously. This is especially true for SHE. Here relativistic effects on the electronic structure become increasingly strong and significantly influence the behavior of these elements. Deviations from the periodicity of chemical properties, based on extrapolations from lighter homologs in the PTE, have been predicted since first Dirac-Fock and Dirac-Fock-Slater calculations were performed in the late 1960s [42, 43]. In more general terms, the issue of "Relativity and the Periodic System of Elements" has been in the focus for some time [82, 83].

In a synergistic interaction, it is one of the top priorities of theoretical – and experimental – studies of SHE to predict – and to validate or contradict – the chemical behavior of SHE, especially in reflection to their position in the PTE. Relativistic quantum-chemical treatments, which reliably calculate the electronic configurations of heavy-element atoms, ions and molecules, – combined with fundamental physico-chemical considerations of the interactions of these species with their chemical environment – now allow detailed predictions of chemical properties of SHE. They are often compared with empirical, linear extrapolations of chemical properties along groups and periods to disclose the impact of relativistic effects. However, these empirical extrapolations are not purely non-relativistic, as relativistic effects are, to some extent, already present in lighter elements. An additional complication for such assessments is the competition between relativistic and shell structure effects. This may obscure a clear-cut correlation between an observed chemical property and one specific effect. It poses an additional challenge for a deeper understanding of the chemistry of elements at the uppermost reaches of the PTE. However, many landmark accomplishments resulted from a number of new and detailed experimental findings and theoretical results over the last decade. For summaries and reviews of the theoretical work see [44–49].

3.2 Relativistic effects

A detailed discussions of relativistic effects in general and specifically for SHE can be found in [82–84] and [44–49], respectively. The relativistic mass of the electron, m, is

$$m = m_0/[1-(v/c)^2]^{1/2}, \tag{1}$$

where m_0 is the electron rest mass, v is the velocity of the electron and c the speed of light. The effective Bohr radius

$$a_\mathrm{B} = \frac{\hbar^2}{mc^2} = a_\mathrm{B}^0\sqrt{1-(v/c)^2} \tag{2}$$

decreases with increasing electron velocity. This orbital contraction and stabilization of the spherical s and $p_{1/2}$ electrons – the direct relativistic effect – was originally thought to be important only for the "fast", inner K and L shell electrons. However, it has been realized that the direct relativistic effect is still large even for the outermost s and $p_{1/2}$ valence electrons in superheavy elements. Thus, *e.g.*, the 7s orbital of element 112 is relativistically stabilized by 6 eV, *i.e.*, doubling the binding energy as compared with the non-relativistic case, and it is 25% contracted [85].

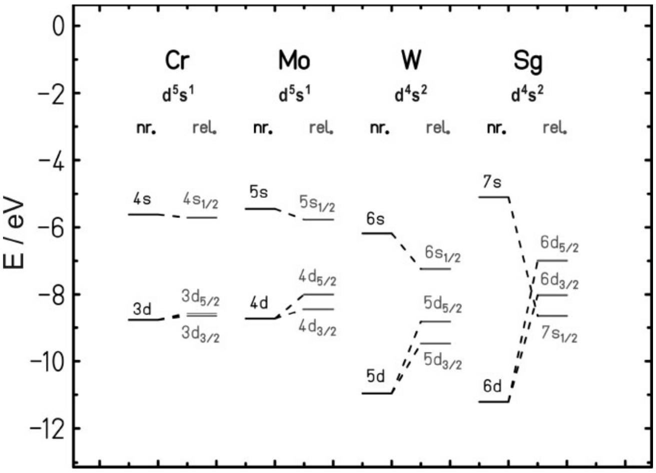

Fig. 3. Relativistic (rel.: Dirac–Fock calculations) and non-relativistic (nr.: Hartree–Fock calculations) energy levels of the group 6 valence *ns* and $(n-l)d$ electrons. Adapted from [25]. Original drawing courtesy V. Pershina.

The second relativistic effect – the indirect relativistic effect – is the expansion of outer d and f orbitals. The relativistic contraction of the s and $p_{1/2}$ shells results in a more efficient screening of the nuclear charge, so that the outer orbitals, which never come close to the core, become more expanded and energetically destabilized. As an example, Fig. 3 shows the stabilization of the ns orbitals, as well as the destabilization of the $(n-1)d$ orbitals, for group-6 elements. One can see the increasingly strong influence of the relativistic effects on the absolute and relative position of the valence orbitals. For element 106, for example, even the level sequence of 7s and 6d orbitals is inverted. It can easily be anticipated that such changes may lead to unusual oxidation states, ionic radii very different from simple extrapolations in a specific group or significant changes in ionic and the covalent portions of chemical bonds.

The third relativistic effect is the spin-orbit (SO) splitting of levels with $l > 0$ (p, d, f, *etc.* electrons) into $j = l \pm 1/2$. This also originates in the vicinity of the nucleus. The SO splitting for the same l value decreases with increasing number of subshells, *i.e.*, it is much stronger for inner shells, and it decreases with increasing l for the same principal quantum number. In transactinide compounds, SO coupling becomes similar, or even larger, in size compared with typical bond energies. The SO splitting of the valence 7p electrons in element 118, *e.g.*, may be as large as 11.8 eV [47]. Each of the three effects (direct and indirect relativistic effect and SO splitting) is of the same order of magnitude and grows roughly as Z^2. That's why it is most fascinating to experimentally probe the highest Z elements.

4. Experimental techniques

Experimental techniques for chemical studies of SHE have to cope with single ions or atoms of short-lived isotopes –

posing most extreme boundary conditions for chemical studies. As a single atom cannot exist in different chemical forms taking part in the chemical equilibrium at the same time the classical law of mass action is no longer valid [86, 87]. For single atoms, the concept of chemical equilibrium is substituted by an equivalent expression in which concentrations, activities, or partial pressures are replaced by probabilities to find an ion, molecule, or atom in one state or the other provided that the exchange is fast enough [88]. The time it spends in one state or another – the measure for its probability to be in either phase – can be determined in dynamical partition experiments. These are characterized by the flow of a mobile phase relative to a stationary phase while a single atom is frequently changing between the two phases. This is realized in many chromatographic separations. Here, retention or elution times provide information about the average time an atom has spent in either phase. Such characterizations of the behavior of a single atom yields information approximating the equilibrium constant that would be obtained from macroscopic amounts of this element. More detailed information on this situation can be found in [25, 54, 56, 60, 61, 89].

Increasingly fast and automated chemical separation techniques were first applied to study short-lived nuclides from nuclear fission; see the companion article [90] in this special issue and [91, 92] for reviews of earlier works. Also the discovery of new chemical elements up to Md ($Z = 101$) – presumably the first one-atom-at-a-time chemistry – was accomplished by chemical means [93] and gas-phase chemistry played an important role in the discovery claims of elements 104 and 105 [3]. Today, the fastest chemical separations have reached the one-second half-life range for studies of SHE. Experimental details and reviews on methods and techniques with varying emphasis can be found in [25, 54, 61, 94–99] and in a comprehensive coverage [100].

Constituents of experiments are (i) nuclear synthesis, (ii) transport to a chemical apparatus, (iii) formation of a desired chemical species (this can be done before, during or after the transport and this is not valid for studies of atomic properties), (iv) fast chemical separation and chemical characterization, (v) preparation of a sample suitable for nuclear spectroscopy (usually not required as an extra step for studies in the gas-phase), and (vi) detection of the nuclide *via* its nuclear decay. SHE chemistry requires stringent optimizations of all of these steps.

The chemical separation system has to fulfill several prerequisites simultaneously [100]. (i) Speed becomes increasingly important when moving from nuclides like 78-s ^{261}Rf to 9.7-s ^{269}Hs and 0.69-s ^{288}114. (ii) A sufficiently high number of exchange steps are required for an individual atom to allow its behavior to be characteristic of the element. (iii) The system needs to be selective enough, not only to probe a specific chemical property, but also to separate unwanted nuclear reaction by-products, which may obscure a unique identification of the atom under investigation. (iv) The observation of a characteristic nuclear decay signature is the only means of identifying a single atom. Thus, in aqueous phase chemistry, samples suitable for α-spectroscopy, need to be prepared after the separation. (v) As today's SHE experiments do not allow a direct identification of chemical species, all systems must be chosen such that a certain chemical state is probable and stabilized by the chemical environment. Only this makes any interpretation of an experimentally observed result meaningful.

4.1 Techniques and instruments for synthesis and transport

Accelerators deliver ion beams, like ^{18}O, ^{22}Ne, ^{26}Mg, and ^{48}Ca, with intensities of $3–6 \times 10^{12}$ s^{-1}, for irradiation of actinide targets with thicknesses up to about 1 mg/cm^2. Provided that a sufficient amount of target material is available, rotating target wheels are prepared to minimize the heat load per unit area from the penetrating particle beam to avoid damage to the target, its backing material, or any window foil. Often a combination of a window and a target backing foil (stationary [101, 102] or rotating), with a flow of cooling gas in between, is used in experiments which directly thermalize and collect recoiling nuclear reaction products in a gas-filled chamber. As these recoil chambers are operated at a pressure of ≈ 1.3 bar, relatively thick window foils are required to withstand the pressure difference to the beam line vacuum. In return, high energy losses result. More details on target design and preparation methods can be found in [103–107]. Common to all of these arrangements is a recoil chamber behind the target. Nuclear reaction products recoiling out of the target are stopped in helium or another gas. Sufficiently volatile products (atoms or chemical compounds) are transported by the flowing gas through capillaries to the chemistry and detector apparatus. For non-volatile products, aerosols – soluble salts, like KCl, for studies in the aqueous phase and carbon "clusters" for gas-phase experiments – are used as a carrier material [100].

Gas-jet technique with aerosol (cluster) particles and a recoil chamber directly behind the target were successfully applied for chemical studies up to Sg [108] and Bh [109]. However, it has at least three severe disadvantages [25, 61, 100, 110–112]. The first one is related to the need of the above mentioned relatively thick window. Because of the large energy loss of beam particles in these foils, *e.g.*, 20 μm Be, and the danger of breaking them, tolerable beam intensities far below the available ones from accelerators restrict production rates. As gas-jets with aerosol particles transport the desired species and unwanted nuclear reaction by-products without any selectivity, this can be seen as a second disadvantage. Usually, a large spectrum of products is very demanding for the chemical separation and for unambiguous nuclear decay identification. A third disadvantage originates from the primary beam passing through the recoil chamber and interacting with the stopping gas. The ionization of this gas is often referred to as "plasma effect". At higher beam intensities, efficiencies of aerosol jets decrease drastically with increasing beam intensities limiting the number of accessible atoms. In addition, the "plasma effect" restricts the accessible SHE compounds to those that are thermally stable; *i.e.*, only inorganic compounds like halides and oxides [25, 58, 61, 62]. Recent approaches to overcome these limitations and to open new perspectives for SHE chemistry are discussed in Sect. 4.2.

Thermally stable, volatile compounds give access to efficient and chemically often very selective transports: the in-situ formation of a volatile compound in the stopping gas behind the target and a cluster-less transport in a pure gas. Chemical investigations of HsO_4 combined with nuclear studies of $^{269-271}$Hs, are prime examples for this approach.

Also species which are volatile in the elemental form can be transported with high efficiency from the recoil chamber to any chemistry device or detector. Here, the chemistry of elements 112 and 114 are outstanding examples. These experiments will be discussed in Sect. 5.

4.2 Physical pre-separators

All three of the above mentioned disadvantages of aerosol-jets with recoil chambers coupled directly to the target can be circumvented by using interjacent physical pre-separators [110–115]. In this most recent development, which constitutes a breakthrough in SHE chemistry, gas-filled magnetic recoil-separators are applied between the target and the recoil chamber - now commonly termed Recoil Transfer Chamber, RTC [116–118]. Pioneering work has been performed at the BGS [113, 116, 119, 120] followed by new developments and experiments at the TASCA [110–112, 121–123], the GARIS [117, 124–127], which had also been used in combination with an IGISOL system before [128], and the DGFRS [129]. A scheme of such a set-up, as used at the GARIS, is shown in Fig. 4.

Actinide targets with thicknesses about 0.5 mg/cm^2, electrodeposited on relatively thin backing foils [104–107], rotate in the filling gas of the separator. Typically, separators are filled with He (H_2 for the DGFRS) at a pressure between 0.4 and 1 mbar; optimized for the separation efficiency. At this pressure, He still acts as a coolant for the target and it allows differential pumping on the beam entrance side to avoid window foils. Both lead to stable operation at beam currents of often more than 1 μA (particle). Separator efficiencies of about 60% for element 114 produced in the ^{48}Ca on ^{244}Pu reaction at TASCA [130] and still 13% for ^{265}Sg synthesized in the very asymmetric ^{22}Ne on ^{248}Cm reaction at GARIS [79] have been reached.

Common to all of these separators is a drastic decrease in efficiency as a function of the nuclear reaction asymmetry because of a larger momentum spread. Recently, at RIKEN a second separator, GARIS-II, was installed with the aim to significantly improve the efficiency. Losses in efficiency, as compared with the use of directly coupled recoil chambers, have often been compensated or even overcompensated by higher beam intensities, higher gas-jet transport yields and more stable operation. Even more important, an increasingly large number of chemical studies profited from much better or unambiguous nuclide identification because of a rigorous background reduction [123]. Some experiments could only identify a nuclear decay signal after pre-separation [113, 118, 119] or were only possible because of the absence of primary beam in the RTC. This paved the way to a completely new class of SHE compounds: metal-organic compounds. Prime examples for this are formation and volatility studies of Hf and Zr complexes with hexafluoroacetylacetone in the preparation of Rf experiments [120] and pioneering experiments with carbonyls [131].

4.3 Techniques and instruments for liquid-phase chemistry

Chemistry with SHE in the liquid phase has been performed mostly in discontinuous, batch-wise operations with a large numbers of cyclic repetitions [25, 60, 132]. While in a few experiments on Rf and Db manual procedures were used [100, 133] most transactinide separations were carried out with the Automated Rapid Chemistry Apparatus (ARCA) [134] and the more advanced Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [135–137]. Both allow fast, repetitive chromatographic separations in miniaturized columns (8 mm long, 1.6 mm i.d.) with typical cycle times between 45 s and 180 s. Depending on the chemistry, columns were filled with cation or anion-exchange resin or an organic extractant on an inert support material. Common to these separations are time-consuming (≈ 20 s) evaporation steps for sample preparation. One of the advantages of AIDA, as compared to its role model ARCA II, is an automation of the sample preparation and mounting. Separation times last typically between 5 s and 10 s.

While ARCA II was most instrumental in many basic chemical studies of Rf and Db in aqueous solution, and allowed the first and so far only liquid-phase experiments with Sg, AIDA facilitated series of very detailed and statistically most significant studies of Rf and various investigations of Db; for details and references see Sect. 5. It was also possible with AIDA to determine an elution curve in liquid chromatography for Rf [138], the first one for a SHE.

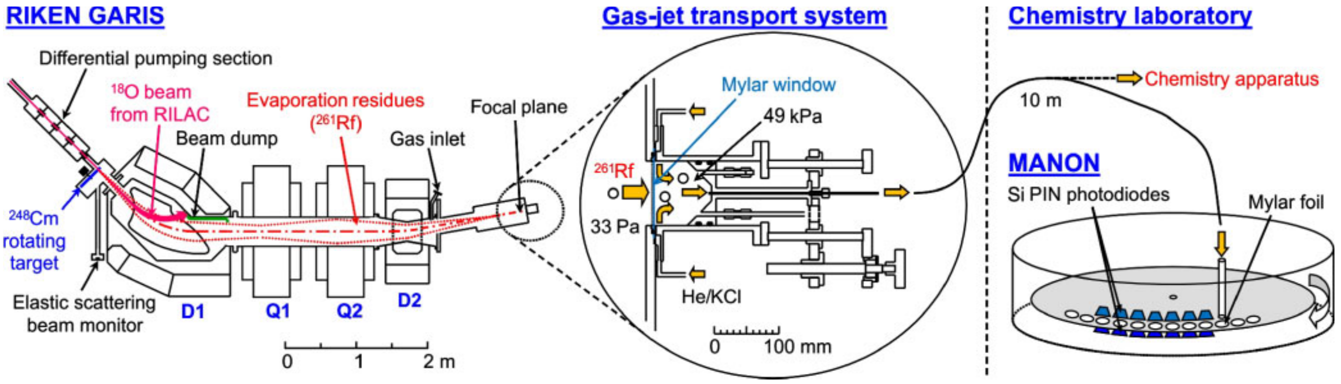

Fig. 4. Coupling of chemistry and rotating-wheel detection devices for α-spectroscopy (MANON) with an RTC (Gas-jet transport system) to the RIKEN GARIS recoil separator (schematically, color on-line). Figure from [126]. Courtesy of H. Haba.

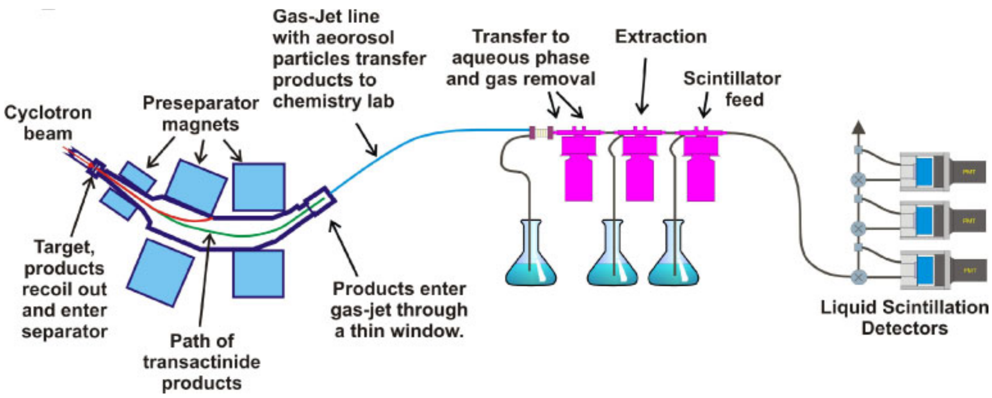

Fig. 5. Flow scheme of SISAK coupled to the BGS in Rf experiments [113]. Drawing courtesy of J. P. Omtvedt.

In the so-called multi-column technique (MCT) continuous or semi-continuous isolation procedures of Rf and its nuclear decay daughter elements, performed on consecutive chromatography columns, were combined with discontinuous sample preparations of long-lived daughter nuclides. An overview of this technique and its application can be found in [60].

A very fast and truly continuous separation and identification technique for SHE became available when the centrifuge system SISAK was coupled to the recoil separator BGS [113, 119, 139]; see Fig. 5. The automated, computer-controlled chemical separation is based on multistage liquid-liquid extractions of aqueous and organic solutions with mixers and consecutive phase separations in miniaturized centrifuges. Several of these stages can be combined according to the needs of a chemical study. Liquid flow rates of ≈ 0.8 mL/s in ^{257}Rf experiments resulted in a total residence time in the 10 and 20 s range. Identification is performed by means of α-liquid scintillation spectroscopy. Because of the large background reduction in the pre-separator, a limited spectroscopic resolution of the order of 300 to 500 keV does not constitute a severe obstacle in these experiments.

4.4 Techniques and instruments for gas-phase chemistry

Transition metals in group 4 to 11 are refractory. However, inorganic compounds, that are appreciably volatile at temperatures below 1100 °C, made gas-phase separation techniques [58, 59, 100] very important in chemical studies of the 6d-elements Rf to Hs [140]. They may also provide means to access elements Mt to Rg. As Cn and the 7p-elements in group 14 to 18 are predicted to be rather volatile in their atomic state, gas-phase studies will, and already are, playing a decisive role in their chemistry; for theoretical predictions see [43, 47–49, 57, 85, 141] and [142] for empirical extrapolations of volatilities.

As recoiling nuclei are stopped in gas, a fast and efficient link can be established to a gas chromatographic system (i) by direct transport of volatile species in the flowing gas, (ii) by formation of a volatile compound in or at the recoil chamber, and (iii) by a transport with cluster (aerosol) particles. Most advantageously, gas-phase separations can be operated continuously. Two types of separations are applied in SHE chemistry: isothermal chromatography and thermochromatography.

Typical for the isothermal chromatography (IC) is that, depending on the temperature of the isothermal column, products are characterized by the time they are leaving the column and their nuclear decay is detected in separate detector behind the column. These experiments make use of the known nuclide half-life to determine a “retention-time-equivalent” to gas chromatographic experiments [95]. On an atom-at-a-time scale, it is the 50% yield value of a breakthrough curve measured as a function of various isothermal temperatures. The temperature corresponding to the 50% yield at the exit of the chromatography column is equal to the temperature at which, in classical gas chromatographic separations, the retention time would be 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 to a detector system. Instead of reclustering, a direct deposition of products leaving the chromatographic column onto thin metal foils was used in some Sg experiments [143] and in a search for element 107 [144].

In gas-solid adsorption thermochromatography (TC) [58, 97, 100], a negative temperature gradient is imposed on a chromatography column. Depending on the temperature range, two different types can be distinguished. For the high temperature version of this method, ranging from about 450 °C to room temperature, only tracks from SF fragments are registered along the chromatography column after the end of the experiment. While this method is fast and highly efficient it has the disadvantage that its temperature range is limited by the fission-track detectors to about 450 °C and, more important, registration of SF fragments is not nuclide specific. This technique was successfully applied in pioneering gas-phase chemistry experiments of Rf and Db by Zvara and coworkers [50, 53, 58, 96, 145, 146]. Continuously operating gas-phase separations – isothermal ones, like the On-Line Gas chromatographic Apparatus (OLGA II) [147], and the ones with temperature gradients – were extremely instrumental in studying the formation of halide and oxide compounds of the transactinides Rf through Bh and to investigate their characteristic retention time – a measure very often expressed as a “volatility”.

The first two low-temperature TC devices were developed and successfully applied in the first chemical separation of Hs [81]. In such devices, the temperature gradient ranges from ambient to liquid nitrogen temperature (−196 °C) and they are well adapted to investigate highly volatile or gaseous species. A great advantage of these devices, named Cryo Thermochromatographic Separator (CTS) [116] and Cryo On-Line Detector (COLD) [81], is that detectors form a chromatographic channel. This allows nuclide identification through α-spectroscopy with almost 100% efficiency and a very good localization of the deposition temperature along the temperature gradient. More recently, a slightly modified version of COLD was applied at the FLNR in Dubna in series of volatility studies of Cn [40, 41, 148] and of element 114 [149]. Presently, the most advanced detector of this type is the Cryo Online Multidetector for Physics And Chemistry of Transactinides (COMPACT). Its TC column consists of two linear arrays of 32 Passivated Implanted Planar Silicon (PIPS) detectors (10×10 mm each), which are facing each other at a distance of 0.5 mm. To probe differences in the adsorption strength of chemical compounds and atoms of SHE with the TC column wall, a variety of detectors with different surface materials, like SiO_2, Al or Au, are available. COMPACT was very instrumental in a large number of chemical and nuclear oriented Hs experiments [72, 80, 150, 151] and, coupled to TASCA, was used for element 114 studies [123, 152].

In IC experiments, volatile chemical compounds are often formed by adding a reactive gas in the hot entrance (reaction) zone ahead of the chromatographic column. But this can also be done in (or at the outlet of) the recoil chamber [58, 96, 153]. The formation of a volatile species in the recoil (or recoil transfer) chamber is typical in TC. The formation and characterization of volatile HsO_4 [81] is an example for such an in-situ volatilization; O_2, acting as a reactive gas, was a component in the transport gas.

Over the last decades, in addition to the above mentioned techniques and devices, several very unique detection systems for highly volatile or gaseous products were developed; among them a cryo-detector [154] for the search for SHE, CALLISTO [155] for a study of HsO_4 interacting from the gas phase with solid sodium hydroxide, OSCAR [156] for a search for ^{272}Hs, and a combination of ionization chamber and neutron-multiplicity detector in an experiment to search for element 112 [157].

5. Chemical properties

Experimental work on transactinides started half a century ago at about the same time when Radiochimica Acta was launched. At first in Dubna and followed in Berkeley, attempts to synthesize element 104 began. Soon, these physical experiments were complemented by chemical studies to determine first chemical properties for a comparison with expected ones from its position in the Periodic Table and to support discovery claims [50–53, 145, 146]. 30 years later, the TWG concluded [3] that “The chemical experiments in Dubna ([145] with [146]) and the Berkeley experiments [158] were essentially contemporaneous and each show that element 104 had been produced. Credit should be shared.”

Already these first experiments showed that element 104 has properties in agreement with its predicted position as the first transactinide and member of group 4 of the PTE [51, 52, 145, 146]. Over about half a century, our knowledge about chemical properties of SHE has advanced significantly. A big leap has been made over the last two decades because of technical developments of automated rapid chemistry and detection techniques and modern, fully-relativistic molecular theories. SHE chemistry has reached a sensitivity that chemical information can be obtained with one atom per day or even week with nuclides live about one second. The architecture of the PTE at its uppermost end, questions about its predictive power as a chemical ordering scheme, and the influence of relativistic effects on chemical properties provide a strong impetus for this research.

Today, there is such a wealth of information available on SHE chemistry that it would go beyond the scope of this article to lay this all out in detail. Comprehensive reviews can be found about the chemistry of superheavy elements [25, 54–57, 61, 62], more specifically also on properties in the aqueous phase [60, 132] and in gas phase [58, 59, 140], and about the state and power of theoretical models and their predictions of chemical properties [44–49]. Therefore, after a very brief introduction to each element, only selected interesting aspects will be discussed in the following.

5.1 Rutherfordium (Rf, element 104)

Pioneering experiments by Zvara and coworkers with experiments in the gas phase [50, 146] and by Silva *et al.* and Hulet *et al.* in acidic, aqueous solutions [51, 52] demonstrated that Rf behaves different from trivalent actinides, and - as expected for a member of group 4 of the Periodic Table – similar to its lighter homologs Zr and Hf. Recent studies of Rf have revealed a number of surprises. In the following, these will be discussed in an exemplary way. Overviews can be found in [25, 54, 56, 57, 61]. Refs. [55, 60, 132] concentrate on Rf properties in the aqueous phase and [58, 99, 140, 146] on the gas phase.

5.1.1 Liquid-phase chemistry

Experiments in the aqueous phase focus on unraveling the competing strength of hydrolysis and complex formation with halide anions. In parallel, and to compare and understand measured distribution coefficients (K_d), theoretical model calculations [57, 159] computed hydrolysis constants and complex formation constants for group-4 elements ($M = Zr$, Hf, Rf); see [25, 60] for more details. For M^{4+} species, which undergo extensive hydrolysis at a $pH > 0$, it was predicted that the hydrolysis decreases in the sequence $Zr > Hf > Rf$. Also the fluoride complex formation of non-hydrolyzed species (present in strong acid solutions) decreases along the group in the sequence $Zr > Hf > Rf$. However, it was realized that this trend is inverted ($Rf \geq Hf > Zr$) at a $pH > 0$ for the fluorination of hydrolyzed species or fluorocomplexes. Under these less acidic conditions differences between the group-4 elements are very small. Chloride complexation was calculated to be independent of pH and always follows the trend: $Zr > Hf > Rf$.

Experimental results about the Rf behavior in comparison with its lighter homologs and pseudo-homologs were obtained (i) from extracting neutral species into tributylphosphate (TBP) and trioctylphosphine oxide (TOPO) with HCl solutions [160–165], (ii) from extractions of anionic complexes with triisooctyl amine (TiOA) with HF and HCl solutions [166, 167], (iii) from ion-exchange studies of predominantly cationic species with HF and HNO_3 solutions [168–171], (iv) from ion-exchange studies of predominantly anionic species with HF, HCl, and HNO_3 solutions [135, 138, 168, 172, 173], from ion-exchange studies of anionic and cationic species with H_2SO_4 and mixed $H_2SO_4/HCLO_4$ solutions [174], and (v) from adsorption experiments on cobalt ferrocyanide [175]. After very briefly summarizing more recent results from experiments with HCl, HNO_3, and H_2SO_4 solution, experimental data obtained over a wide range of HF concentrations, and their interpretation, will be discussed. A comprehensive discussion of all experiments performed in the aqueous phase can be found in Ref. [60].

In recent experiments, Rf and its lighter homologs were observed after passing through column chromatographic separations. After first results from ARCA II, these studies were predominantly carried out with AIDA at the Japan Atomic Energy Agency (JAEA) Tandem accelerator in Tokai, Japan [137]. MCT experiments probing the behavior of cationic species of Rf in dilute HF and mixed HF/HNO_3 solutions yielded results which are in agreement with the quantitative studies of ARCA and AIDA; see [60]. Rf experiments with SISAK coupled to the BGS pioneered this technique for continuous liquid SHE chemistry [113, 139]. Rf was extracted from 6 M HNO_3 into 0.25-M dibutylphosphoric acid (HDBP) in toluene [113]. From sulphuric acid solution into trioctylamine, Rf extracts to a lesser extent than Zr, and probably also slightly less than Hf [139]. This is in accordance with theory predicting the extraction sequence Zr > Hf > Rf [176]. In all experiments, except for a study in H_2SO_4 [174], kinetics was assumed to be fast enough to establish equilibrium conditions.

The sulfate complexation of Rf was studied in mixed H_2SO_4/HNO_3 solutions on cation-exchange resins in AIDA [174]. It was found that the Rf adsorption probability decreases with increasing HSO_4^- concentration showing a successive formation of Rf sulfate complexes similar to the behavior of Hf. However, Rf exhibits a weaker complex formation tendency compared to Zr and Hf. This is in good agreement with theoretical predictions including relativistic effects [176]. Contrary to any other experiment, this sulfate complexation study indicated slow exchange kinetics specifically for the lighter homolog Zr. Differences in the adsorption strength between Zr and Hf were attributed to a non-equilibrium behavior of Zr. All data for Hf indicated that it has reached equilibrium conditions. The reason for the Zr behavior is presently not understood.

A hypothetically Th-like or Pu-like behavior of Rf was excluded in AIDA with an anion-exchange resin and 8 M HNO_3 [135]. While anionic complexes of Th and Pu(IV) strongly adsorbed, Rf remained in solution.

Neutral MCl_4 complexes (M = Zr, Hf, Rf) were characterized by extracting Zr, Hf and Rf from HCl into tri-*n*-butyl phosphate (TBP) and trioctylphosphine oxid (TOPO). Column chromatographic separations with TBP were performed from 8 M HCl in ARCA [162, 163], while experiments in AIDA used 7.2–8.0 M HCl with TBP [164] and 2–7 M HCl with TOPO [165]. The AIDA experiments obtained extraction sequences of Zr > Hf ≈ Rf into TBP and Zr > Hf ≥ Rf into TOPO. This suggests that the stability of $RfCl_4(TBP)_2$ and $RfCl_4(TOPO)_2$ complexes may be lower than those of the Zr and Hf ones [164, 165]. No theoretical calculations are available for the TBP and TOPO systems. In agreement with off-line data ($K_d(\mathrm{Hf}) = 65$, $K_d(\mathrm{Zr}) = 1180$), column chromatographic separations with TBP in ARCA yielded a distribution coefficient of (150^{+64}_{-46}) for Rf as compared to (53^{+15}_{-13}) for Hf [162]. From the extraction sequence Zr > Rf > Hf, the same sequence was concluded for the strength of the MCl_4 complex. This possibly surprising sequence is not in contrast with theoretical considerations on the competition between hydrolysis of the chloro complexes and the formation and the extraction of these complexes into the organic phase [159, 162]. Presently, differences in the sequence of Rf and Hf extractions between ARCA and AIDA experiments remain unexplained.

The formation of anionic chloride complexes from concentrated acid solutions was studied in anion-exchange chromatographic separations with AIDA [124, 135, 177]. They show that the adsorption of Rf (measured as percent adsorption) increases steeply from 7 to 11.5 M HCl. Typical for a group-4 element, this behavior goes in parallel with that of Zr and Hf, and is different from that of Th. The observed adsorption sequence of Rf > Zr > Hf is also interpreted as the sequence in chloride complexing strength. However, this outcome remains to be understood theoretically as it contradicts earlier predictions [159].

Theory predicts that, for cation-exchange separations in dilute ($< 10^{-2}$ M) HF, the K_d-values will have the following trend: Zr ≤ Hf < Rf. This reflects the above mentioned decreasing trend Zr ≥ Hf > Rf in the formation of positively charged complexes. To investigate the successive F^- complex formation of cationic species, the behavior of Zr, Hf, Th, and Rf in mixed 0.1 M HNO_3/HF solutions was studied in cation-exchange chromatography experiments with ARCA [168]. For Zr and Hf, K_d-values drop from 10^{-4} M to 10^{-2} M HF. Rf shows this at about one order of magnitude higher HF concentrations, and it appears at even higher concentrations for Th. This establishes the following sequence of F^--complex formation strength at low HF concentrations: Zr ≥ Hf > Rf > Th. For a similar system confirming data were obtained with AIDA [169] and, more

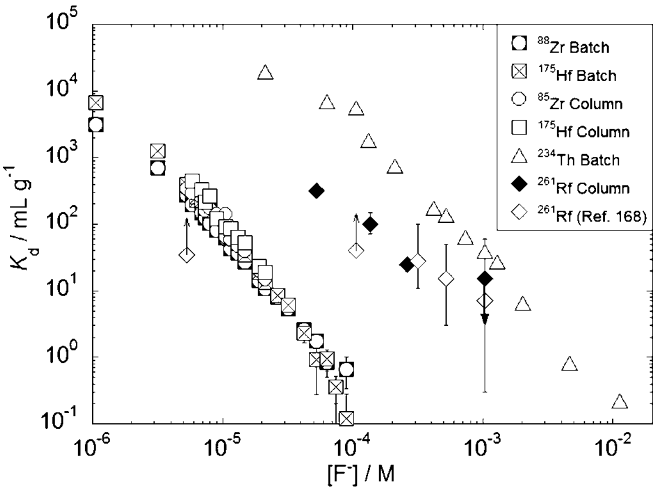

Fig. 6. Distribution coefficients (K_d) on cation-exchange resins in 0.1 M HNO_3 as a function of the free fluoride ion concentration. Figure adapted from [170]. Courtesy of A. Toyoshima.

recently, very precise adsorption measurements as a function of F^- ion concentration confirmed these findings [170, 171]; see Fig. 6. A most recent study found that the same chemical species MF^{3+}/MF_2^{2+} of Rf and its homologs are present and adsorbed on the cation-exchange resin.

Qualitatively, the experimentally observed sequence of extraction and complex formation is in good agreement with theoretical expectations [159]. Predicting K_d values quantitatively, still remains a challenge for theory because of a large variety of positively charged complexes in solution and extracted. However, using the ionic radii [178] of Zr (72 pm), Hf (71 pm), Rf (76–78 pm, calc.), and Th (94 pm) it is suggestive to apply the empirical Hard Soft Acid Base (HSAB) concept [179] to explain the observed extraction sequence. In this concept one assumes that the hard F^- anion interacts stronger with small (hard) cations. From this, one expects, in agreement with the observation, a weaker F^- complexation of Rf as compared with Zr and Hf.

The experimental situation concerning the transition towards anionic species at HF concentrations from 10^{-2} M to 1 M HF in mixed HF/HNO_3 solutions started somewhat surprising. In an experiment with an anion-exchange resins [168], K_d values increase from ≈ 10 to more than 100 from 10^{-3} M to 10^{-1} M HF for Zr and Hf (measured off-line in batch extractions with long lived tracers). This is consistent with a continuation of the trend observed on cation-exchange resin. For the Th off-line data, and for Rf on-line data, no significant rise of the K_d values was observed from 10^{-3} M HF up to 1 M HF. While this is expected for Th, it came as surprise for Rf. However, follow up experiments showed for Hf a significant and for Rf an even much more pronounced dependence of the adsorption probability on NO_3^- and HF_2^- counter ion concentrations [180]. While for Hf distribution coefficients (K_d) of $\log K_d > 2$ were found in a wide range of concentrations from 0–0.1 M HNO_3 and 0.01–1.0 M HF, such high values were found for Rf in 0.01–0.1 M HF only with no nitric acid added.

The formation and adsorption of MF_6^{2-} complexes of Zr, Hf, and Rf was studied in detail with AIDA on an anion-exchange resin at low fluoride ion concentration taking into account the influence of NO_3^- and HF_2^- counter ions [173]. RfF_6^{2-} formed in the studied range of 0.0005 to 0.013 M of equilibrated $[F^-]$, but the formation of the Rf complex was significantly different from the Zr and Hf one. The formation constant of RfF_6^{2-} is at least one order of magnitude smaller than those of ZrF_6^{2-} and HfF_6^{2-}. In moderate qualitative agreement with a fully-relativistic density-functional theory calculation [159], formation constants (K_6) of <100, 1900, and 3200 were determined for Rf, Zr, and Hf, respectively, from modeling the experimental results. From an analysis of the K_d-value dependence as a function of NO_3^- concentration, *i.e.*, from the exchange reaction between RfF_6^{2-} and the NO_3^- counter ion on the ion-exchange resin, a slope of −2 was determined; see Fig. 7. This confirmed the existence of RfF_6^{2-}, similar to ZrF_6^{2-} and HfF_6^{2-}, in the studied range of fluoride concentrations.

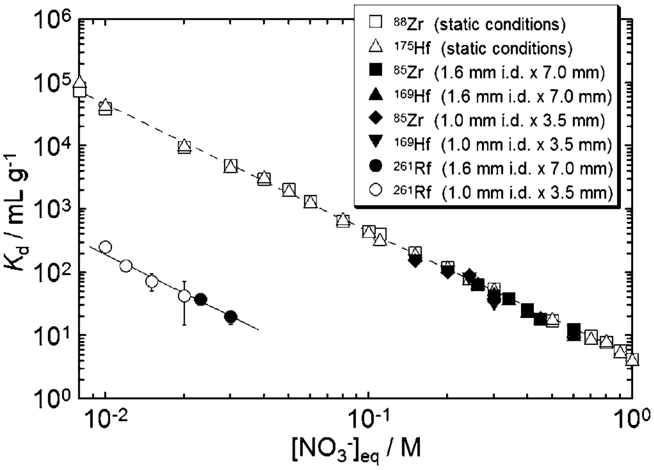

Fig. 7. Distribution coefficients (K_d) of Zr and Hf obtained under static conditions and of Zr, Hf, and Rf from anion-exchange column chromatography as a function of the $[NO_3^-]$ counter-ion concentration at a constant fluoride concentration of 3.0×10^{-3} M $[F^-]$. Figure from [173]. Courtesy of A. Toyoshima.

Fluoride complexation was also studied by anion-exchange chromatography at higher acid concentrations from 1.9 to 13.9 M HF solution [172]. Here, the $[HF_2^-]$ is increasing approximately like the "initial" [HF] while the $[F^-]$ is almost constant. A decrease of the K_d values of Zr and Hf with [HF] is explained as the displacement of the metal complex from the binding sites of the resin with HF_2^-. It is stunning to see that, in contrast to the experimental results obtained in HCl and HNO_3 solutions, Rf behaves distinctively different from Zr and Hf. Above 2 M HF the percent adsorption on anion-exchange resin drops much earlier for Rf and is significantly less than that of Zr and Hf up to 13.9 M HF. A plot of K_d values *vs.* the "initial" HF acid concentration also revealed a significant difference between Rf and Zr and Hf. A slope of -2.0 ± 0.3 of $\log K_d$ against log[HF] was determined for Rf while the one for Zr and Hf is -3.0 ± 0.1, indicating that different anionic fluoride complexes are formed. The slope analysis indicates that Rf is present as the hexafluoride complex RfF_6^{2-} – similar to the well known ZrF_6^{2-} and HfF_6^{2-} at lower [HF] – whereas Zr and Hf are presumably present in the forms of ZrF_7^{3-} and HfF_7^{3-}.

The capabilities of AIDA were demonstrated in the first elution curve measurement of a superheavy element in liquid chromatography [138]. Rf was eluted in 5.4 M HF from a 1.6 mm i.d. × 7 mm anion-exchange column. The K_d value determined from the Rf elution position is in very good agreement with previously mentioned results [172].

Last decades very reliable and consistent data on the F^- complexing strength of Rf as compared with Zr, Hf, and Th, can be summarized in the following way: (i) Typical for a group-4 element, Rf forms anionic fluoride complexes. (ii) Rf has a much weaker tendency to form anionic F^- complexes as compared with Zr and Hf. It often shows an intermediated behavior between Zr and Hf on one side and Th on the other side. (iii) At increasing (but low: $0.0005\,\text{M} \leq [F^-] \leq 0.013\,\text{M}$) fluoride concentration, RfF_6^{2-} anionic complexes are formed in consecutive complex formation steps, similar to ZrF_6^{2-} and HfF_6^{2-}. The formation constant of RfF_6^{2-} is at least one order of magnitude smaller than those of ZrF_6^{2-} and HfF_6^{2-}. (iv) At high HF concentration, still RfF_6^{2-} is formed as compared to ZrF_7^{3-}.

The experimental finding of a fluoride complex formation sequence of Zr ≥ Hf > Rf is in very good agreement with relativistic molecular density functional calculations [159] of various hydrated, hydrolyzed, and fluoride complexes, where the free energy change for various steps of fluorination was compared for those elements. Due to the predominately electrostatic interaction in the F^- complexes one can also observe in sorption data of MF^{3+} and $MF_2{}^{2+}$ a correlation (a reverse dependence) between crystallographic ionic radii – Zr (72 pm) $\approx$ Hf (71 pm) $<$ Rf (76 pm, calculated) $\ll$ Th (94 pm) – and the complex formation strength [170].

5.1.2 Gas-phase chemistry

With the exception of one experiment [181], which obtained results consistent with earlier works, no new data were acquired on the Rf gas-phase chemistry in recent years. As several comprehensive articles are describing the available results [25, 58, 59, 99, 140, 182, 183], only selected aspects will briefly be mentioned here.

Pioneering Rf experiments in the gas phase (see [50, 146] and [184] concerning the element's name) demonstrated that Rf, similar to Hf, forms a chloride that is much more volatile than the actinide chlorides. After technical advancements, new series of on-line gas-chromatographic studies were performed in the 1990s using chlorinating [185] and brominating [186] reagents; see [99, 140] for reviews. Besides the aim of determining the formation and behavior of Rf compounds, it was the scope of these experiments to probe the influence of relativistic effects on chemical properties [183]. This system seems to be especially apt to obtain a clear answer about the influence of relativistic effects on a chemical property. From relativistic calculations [187], $RfCl_4$ was predicted to be more volatile than $HfCl_4$, whereas from non-relativistic calculations [187] and from extrapolations of trends [142] within the Periodic Table, exactly the opposite behavior is expected.

Because nuclides with very different half-lives were used – a parameter which can strongly influence thermochromatographic results [97, 188] – it was almost impossible to precisely determine relative volatilities in the pioneering experiments. Recently, isothermal gas-chromatographic experiments established a higher volatility of Rf chlorides as compared with Hf chlorides [183, 185, 189]. This has been interpreted as the result of relativistic effects. The somewhat unexpected behavior of Zr chloride, which under similar experimental conditions was observed together with Rf instead of Hf, remains puzzling. A study of Rf bromides showed the same sequence in volatility with Rf bromide being more volatile than Hf-bromide [186, 189].

In Monte Carlo simulations of the chromatographic process adsorption enthalpies ($\Delta H_a^0(T)$) for single molecules on the column quartz surface are obtained by searching a best fit to the experimental data and varying ΔH_a as the free parameter [99, 188]. A compilation ([133] and Fig. 20 in [25]) of group-4 element chloride and bromide adsorption enthalpies shows Zr $\approx$ Rf $>$ Hf – for Rf a striking reversal of the (empirically) expected trend, however, in agreement with relativistic theoretical model calculations [46]. Therefore, this "reversal" is evidence for relativistic effects.

One complicacy when studying pure halides is the possible formation of oxide halides. It was shown in the chloride system that small amounts of O_2 can lead to the formation of a less volatile oxide chloride instead of the pure chloride. This poses problems in the interpretation of experimental results, especially in case of pronounced differences in the trendency Zr, Hf, and Rf form oxide chlorides [183]. Oxide halides are less volatile than pure halides. Such a behavior was first observed in a TC experiment [183]. It is interesting to note, that $RfOCl_2$ and $HfOCl_2$ behave much more similar than the pure halides. This may be connected to the assumption that oxide chlorides are only present in the adsorbed state and not in the gas phase. This would require a transport mechanism [140] in the chromatographic process which includes the formation and breaking of chemical bonds in a molecule (reaction gas chromatography).

5.2 Dubnium (Db, element 105)

In the PTE element 105, dubnium, Db, (see [190] for element 105 names) is placed in group 5 below Nb and Ta. Early TC separations of volatile chloride and bromide compounds showed that Db behaves more like a transactinide than an actinide element [53, 96]. These experiments indicated that Db chloride and bromide are less volatile than the Nb halides [53]. However, a most recent experiment shows a high volatility for the Db bromide. This can be taken as evidence for the formation of less volatile oxide bromides in earlier experiments. In its first aqueous chemistry, Db was adsorbed onto glass surfaces from HCl and HNO_3 solutions, a behavior very characteristic for group-5 elements [191]. However, an attempt to extract Db fluoride complexes failed under conditions in which Ta extracts but Nb does not. This provided evidence for unexpected Db properties [191]. It triggered follow-up investigations with ARCA, recently with AIDA, which revealed unanticipated Db properties when comparing it with its lighter homologs Nb and Ta and with its pseudo-homolog Pa. Except for a few recent studies with AIDA [192, 193] and one on bromide volatilities (see Sect. 5.2.2), no new chemical information was obtained in recent years. As several reviews are describing the experimental results [25, 54, 61, 62, 94], some with emphasis on the aqueous phase [55, 60, 132] or the gas phase [58, 59, 99, 140, 182], only selected examples of the Db chemistry will be presented here. The status of the theoretical work, with comparison to experimental results, is summarized in [47–49, 57, 85].

5.2.1 Liquid-phase chemistry

The first detailed comparison between Db, its lighter homologs Nb and Ta, and the pseudo-homolog Pa was carried out for anionic species formed in solutions at different HCl concentrations – with small amounts of HF added – and triisooctylamine (TiOA) as a stationary phase on an inert support [194]. As expected, complete extraction of Nb, Ta, Pa, and Db into TiOA was found from 12 M HCl/0.02 M HF and from 10 M HCl, respectively. At 4 M HCl/0.02 M HF, it came as a big surprise, that Db followed Nb and Pa and not Ta. At 6 M HNO_3/0.0015 M HF, Db showed an intermediate behavior between Pa and Nb indicating that the halide complexing strength of Db is in between that for Nb and Pa. At 0.5 M HCl/0.01 M HF, Db even showed more Pa-like properties [195]. These stunning results provided strong motivation to investigate Db further. The interpretation of these results was hampered by the use of mixed HCl/HF solutions. In contrast to the experimental result, the inverse order $\mathrm{Pa} \gg \mathrm{Nb} \geq \mathrm{Db} > \mathrm{Ta}$ was theoretically predicted [196] for pure HCl. This work considered the competition between hydrolysis [197] and chloride complex formation. In agreement with theory, a follow-up experiment with Aliquat 336 (Cl^-) and pure 6 M HCl determined an extraction sequence of $\mathrm{Pa} > \mathrm{Nb} \geq \mathrm{Db} > \mathrm{Ta}$ [198].

In pure HCl, at concentrations above 2–4 M, Nb, Ta, Pa, and presumably Db, form the same type of complexes, $\mathrm{M(OH)_2Cl_4}^-$, $\mathrm{MOCl_4}^-$, $\mathrm{MOCl_5}^{2-}$, and $\mathrm{MCl_6}^-$ ($\mathrm{M} = \mathrm{Nb}$, Ta, Db, Pa) with increasing HCl concentrations. From theoretically and experimentally determined strengths of Cl^-complex formation one can say that Pa forms a specific complex in a more dilute solution (starting with $\mathrm{Pa(OH)_2Cl_4}^-$ at 2–4 M HCl) followed by the other elements at higher concentrations. The complexes of Nb start to form next ($\mathrm{Nb(OH)_2Cl_4}^-$ above 4–5 M HCl), while the $\mathrm{Ta(OH)_2Cl_4}^-$ complex is formed at or above 6 M HCl. This suggests that at 6 M HCl the complex $\mathrm{Db(OH)_2Cl_4}^-$ is prevailing.

Additional experiments with HF and HBr solutions [198] confirmed the theoretically expected sequence of complexing strength among the halide anions: $\mathrm{F}^- \gg \mathrm{Cl}^- > \mathrm{Br}^-$. In agreement with theoretical predictions including relativistic effects [199], experiments in 4 M HF [198] show a high Db extraction probability into Aliquat 336 very similar to the Nb and Ta one, and very different from Pa. It was suggested that the complex $\mathrm{DbF_6}^-$ or $\mathrm{HDbF_7}^-$ is formed while Pa forms multi-charged complexes like $\mathrm{PaF_7}^{2-}$ and $\mathrm{PaF_8}^{3-}$.

A recent study in more dilute, mixed 0.31 M HF/0.1 M $\mathrm{HNO_3}$ solution determined a sequences of $\mathrm{Ta} \gg \mathrm{Nb} \geq \mathrm{Db} \approx \mathrm{Pa}$ for the adsorption on an anion-exchange resin [193]. This suggests that, like Nb, the complex $\mathrm{DbOF_4}^-$ is formed which is different from $\mathrm{TaF_6}^-$. From the similarity with Pa, however, formation of multi-charged ions like $\mathrm{DbOF_5}^{2-}$ and $\mathrm{DbF_7}^{2-}$ was not excluded. The inversion of the sequence of adsorption and extraction probabilities of Ta, Nb, and Pa on an anion-exchange resin from 0.31 M HF/0.1 M $\mathrm{HNO_3}$ [193] and into Aliquat 336 from 0.5 M HF [198] was not discussed in [193]. Earlier work [200], however, indicates that this is due to the presence of 0.1 M $\mathrm{HNO_3}$.

Investigations in 13.9 M HF [192] obtained an adsorption strength of $\mathrm{Ta} \approx \mathrm{Nb} > \mathrm{Db} \geq \mathrm{Pa}$ on an anion-exchange resin; an equivalent sequence was observed in group 4 [172]. Similar to Rf in group 4, Db exhibits a significantly weaker tendency to form fluoride complexes than Nb and Ta.

5.2.2 Gas-phase chemistry

Summaries of Db gas phase chemistry are given in [25, 58, 59, 61, 99, 140, 182, 189]. Volatilities of Db and group-5 elements have been studied with pentahalides (chlorides and bromides) and with the less volatile oxide halides. A strong tendency of group-5 elements to react with trace amounts of oxygen or water to form oxide halides [58, 99, 182], make studies of pure halides challenging, and, because of surface reactions, may prevent the use of quartz columns. Some data and their interpretation may suffer from an unintentional and unrecognized formation of oxide halides.

For Db homologs, the following trends have been observed: (i) The volatility of $\mathrm{MX_5}$ decreases in the sequence $\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I}$, which can be compared with $\mathrm{Cl} > \mathrm{Br} > \mathrm{I} > \mathrm{F}$ in group 4. (ii) Oxide halides are less volatile than the corresponding halides, which is also true in group 4. (iii) Group 5 halides have an equal or even higher volatility than the corresponding ones in group 4. Some of these comparisons may still be affected by unclear assignments to pure halides or oxide halides. A discussion of these properties from a theoretical point of view can be found in [46–48].

Early experiments in chlorinating and brominating atmospheres showed that Db formed compounds which were less volatile than the Nb ones [53]. The lower volatility of a Db compound as compared to the lighter homologs Nb and Ta was again seen in a IC experiment with OLGA carried out in a brominating environment [201]. From this, a trend in volatility of $\mathrm{Nb} \approx \mathrm{Ta} > \mathrm{Db}$ was concluded. This is surprising since theoretical calculations, including relativistic effects, predict a higher volatility for $\mathrm{DbBr_5}$ as compared to $\mathrm{NbBr_5}$ and $\mathrm{TaBr_5}$ [46, 202]; similarly to the observed sequence in group 4. It was speculated [99] that instead of the pentabromide the $\mathrm{DbOBr_3}$ may have been formed. However, this implicates that, under identical conditions, Nb and Ta form pentabromides while Db forms an oxide bromide. Recently, a fully-relativistic calculation introduces a new aspect into the discussion. For the pentabromides, it predicts a volatility sequence of $\mathrm{Nb} < \mathrm{Ta} < \mathrm{Db}$ in case of a van-der-Waals type of interaction with the wall material but the inverse sequence of $\mathrm{Db} < \mathrm{Ta} < \mathrm{Nb}$ in case of chemical bond formation [203]. A recent experiment, which shows a high volatility for Db bromide [204], can be taken as evidence for the formation of less volatile oxide bromides in earlier experiments. It leads to a revision of bromide volatilities within the group-5 elements, now with $\mathrm{DbBr_5}$ being the most volatile one. This does not contradict theoretical calculations [205] showing a stronger tendency for Db to form oxide halides than Nb and Ta and could be viewed as an influence of relativistic effects in Db. A different theoretical approach showed a monotonic trend in the series of Nb, Ta and Db for the stability of monooxides [206].

Several attempts failed to form the pure $\mathrm{DbCl_5}$. Experiments with OLGA, using elaborated purification techniques, established a break-through curve for $\mathrm{NbCl_5}$. However, Db showed a behavior, which was interpreted as the result from two species present, namely $\mathrm{DbCl_5}$ and $\mathrm{DbOCl_3}$ [99]. Compared to $\mathrm{NbOCl_3}$, $\mathrm{DbOCl_3}$ became “volatile” at an approximately 50 °C higher temperature – indicating a lower volatility for $\mathrm{DbOCl_3}$ as compared to $\mathrm{NbOCl_3}$. For, what was interpreted as a $\mathrm{DbCl_5}$ component, only a volatility limit was established. A final comparison of halide volatilities of all group 5 elements remains to be performed.

5.3 Seaborgium (Sg, element 106)

For 20 years, since its discovery in 1974 [207], 0.9-s $^{263}\mathrm{Sg}$ was the longest-lived Sg isotope. Its short half-life prohibited chemical investigations. With the firm belief that one would be able to produce the hitherto unknown, longer-lived isotopes $^{265,266}\mathrm{Sg}$ in a $^{22}\mathrm{Ne} + {}^{248}\mathrm{Cm}$ reaction, preparations started in the early 1990s to investigate Sg in the aqueous and in the gas phase. Finally, in the mid 1990s, a large international collaboration of 16 institutes from nine countries performed the so far only series of Sg chemistry experiments at the GSI, Darmstadt, which yielded today's knowledge about Sg chemistry [108, 208–212]. First observed at the DGFRS by a Dubna-Livermore collaboration [213, 214], ^{265}Sg was used in the Sg chemistry. Interpretation of a ≈ 20-s SF decay component, also observed in these experiments, to be ^{266}Sg was recently shown to originate from a short-lived isomeric decay in the ^{265}Sg daughter nucleus ^{261}Rf [79, 215]. The ^{22}Ne + ^{248}Cm reaction produces two states of ^{265}Sg with half-lives of 9 and 16 s, respectively [79, 215]. They will also be used in presently prepared, future Sg experiments.

Sg is expected to chemically behave like a member of group 6 of the Periodic Table with Cr, Mo and W as the lighter homologs. Oxides, oxide halides and hydroxide halides are important and characteristic compounds of these elements. The formation and the properties of such Sg compounds, in comparison with lighter homologs, have been investigated in the aqueous phase and in the gas phase. A comprehensive description of the Sg experiments is given in [25] and the above mentioned original articles. In the following, this will briefly be summarized.

5.3.1 Liquid-phase chemistry

Chemical separations and characterizations of Sg in aqueous solution [108, 208, 209], conducted on cation-exchange resins in ARCA II [134], probed the Sg behavior in comparison with its lighter group-6 homologs Mo and W. It also aimed at distinguishing it from hexavalent U. In the first experiment, performed in 0.1 M $HNO_3/5\times10^{-4}$ M HF, three correlated α-α-decays of ^{265}Sg daughter nuclei were detected. From this it was concluded [108, 208] (i) that Sg elutes together with Mo and W, (ii) that it behaves like a typical group-6 element and forms hexavalent ions, (iii) that, like its homologs Mo and W, Sg forms neutral or anionic oxide or oxide halide compounds, and (iv) that it does not form seaborgyl ions (SgO_2^{2+}) – different from its pseudo-homolog U which remains as UO_2^{2+} on cation exchange resins. By analogy with Mo and W, it can be assumed that Sg is forming a (hydrated) anionic complex like $SgO_2F_3^-$ or the neutral species SgO_2F_2. Such properties are typical for group-6 elements – but not for U.

As the formation of seaborgate ions (SgO_4^{2-}) was not entirely excluded, a second experiment was performed with pure 0.1 M HNO_3 [209]. Contrary to Mo and W, Sg was not eluted in the absence of HF. From this, it is concluded that F^- anions contributed to the complex formation in the first experiment. This indicates that Sg was not eluted as SgO_4^{2-}in the first experiment. The non-tungsten like behavior of Sg in pure HNO_3 may be attributed to its weaker tendency to hydrolyze [209, 216, 217]. 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 $SgO(OH)_3^+$) or already even at $Sg(OH)_4(H_2O)_2^{2+}$. This trend in the hydrolysis of metal cations is not only theoretically predicted for group 6 ($Mo > W > Sg$) but also for group 5 ($Nb > Ta > Db$); see [47, 48] for predicted and observed hydrolysis sequences. A detailed discussion of the behavior of Sg in aqueous solution can be found in [60].

5.3.2 Gas-phase chemistry

As a member of group 6, Sg is expected to be very refractory in the elemental state but to form volatile halides, oxide halides, oxide hydroxides, and carbonyls [131, 218]. While only a very limited number of relatively unstable hexahalides exist in group 6, a much larger variety of more or less stable oxide halides of the types MOX_4 and MO_2X_2 ($M = Mo$, W; $X = F$, Cl) are known. The formation and volatility of oxide halides of Sg was probed in comparison with Mo and W [108, 211]. Presumably, $SgO_2(OH)_2$ was synthesized [212]. After a revision of nuclear decay properties [215], today we know that all Sg chemistry experiments at GSI used the isotope ^{265}Sg. A discussion of relative stabilities and volatilities of group-6 compounds can be found in [140, 142, 219] from an empirical point of view and in [47, 187, 220, 221] based upon relativistic theory. The latter includes aspects of the stability of the predominant hexavalent oxidation state in Sg. It is worthwhile mentioning attempts at Dubna to chemically investigate Sg in a high temperature TC approach using the 0.9-s SF-isotope ^{263}Sg [222]. Because of difficulties mainly caused by the use of ^{263}Sg, no information on the Sg behavior as compared with Mo and W was deduced from this experiment; see also discussions in [25, 56, 61, 140].

Isothermal gas-adsorption chromatography experiments at the GSI [108, 211] used the OLGA [147] and Cl_2, saturated with $SOCl_2$, and traces of O_2 as reactive gases to study the formation and volatility of the presumably formed dioxide dichlorides. Break-through curves, measured for Mo, W, and Sg compounds between about 150 and 300 °C, reflect the sequence in volatility of $MoO_2Cl_2 > WO_2Cl_2 \approx SgO_2Cl_2$. Monte Carlo simulations gave adsorption enthalpies of $-\Delta H_a(MoO_2Cl_2) = 90 \pm 3$ kJ/mol, $-\Delta H_a(WO_2Cl_2) = 96 \pm 1$ kJ/mol, $-\Delta H_a(SgO_2Cl_2) = 98 + 2/-5$ kJ/mol; the first thermochemical property of Sg determined [211]. Thus, it was shown that Sg forms oxide chlorides analogous to those of Mo and W; different from UCl_6, which has a much higher volatility. This Sg behavior is in line with extrapolations in group 6 and with relativistic theory calculations [221]. A detailed discussion of the thermochemical characterization of Sg is given in [219]. From empirical correlations, a sublimation enthalpy of a hypothetical Sg metal was estimated [211]. If valid, Sg metal would have an equally high or even higher sublimation enthalpy than W. Hence, Sg is one of the least or the least volatile element in the PTE [140].

Because of a strong tendency of group-6 elements to form oxides, no attempts were made to study pure halides. However, studies of moderately volatile oxide hydroxide compounds of Sg were performed in high-temperature (≈ 1000 °C) IC experiments [143, 212]. An O_2/H_2O gas mixture was used as a reactive gas. From preparatory experiments [223] with Mo and W it was expected that also for Sg the slow, dissociative adsorption and associative desorption process called “reaction gas-chromatography” ($MO_2(OH)_{2(gas)} \Leftrightarrow MO_{3(ads)} + H_2O_{(gas)}$) would occur. From the observation of only two Sg atoms passing through the column, it was shown that Sg forms the volatile oxide hydroxide $SgO_2(OH)_2$, a property typical for group-6 elements [212].

5.4 Bohrium (Bh, element 107)

As member of group 7 of the PTE, Bh is expected to have properties similar to its lighter homologs Mn, Tc, and Re. Typical for these elements is the formation of relatively volatile oxides, oxide hydroxides, and oxide halides. Fully relativistic calculations [224] of the electronic structure of the oxide chlorides MO_3Cl (M = Tc, Re, Bh) show that BhO_3Cl is the most covalent one and relatively stable. Theory predicts [224] the following sequence of volatilities: $TcO_3Cl > ReO_3Cl > BhO_3Cl$. The same order results from classical extrapolations of thermochemical properties which also predict BhO_3Cl to be more stable and volatile than TcO_3Cl and ReO_3Cl [225]. These oxide halide compounds of group-7 elements reflect their intermediate position between the lighter transactinides, which form volatile halides, and the highly volatile group-8 tetroxides.

As oxides and oxide hydroxides are also relatively stable and volatile compounds in group 7, attempts to chemically investigate $BhO_3(OH)$ were made, but failed because of insufficient sensitivity [144, 226]. So far, the only information on chemical properties of Bh was obtained in isothermal gas chromatographic experiments on the oxide chlorides performed by Eichler and coworkers at the PSI Philips cyclotron in Villigen [109]. The experimental set-up for separation of 17-s ^{267}Bh, was similar to the one used in the Sg experiments. A remarkable aspect of the Bh experiment was the use of C-aerosols. They were "burned" to CO_2 by the HCl and O_2 containing reactive gas when hitting the 1000 °C hot quartz wool filter.

Break-through yields were measured as a function of the isothermal temperature in the quartz chromatography column. Compounds leaving the IC column were transported with CsCl as a re-cluster material to the detection system. A total of six genetically linked ^{267}Bh decay chains were observed [109]; four at 180 °C, two at 150 °C and none at 75 °C. This result is shown in Fig. 8 as (normalized) relative yields together with data from tracer experiments and with Monte Carlo simulations using a microscopic model [188] to determine standard adsorption enthalpies.

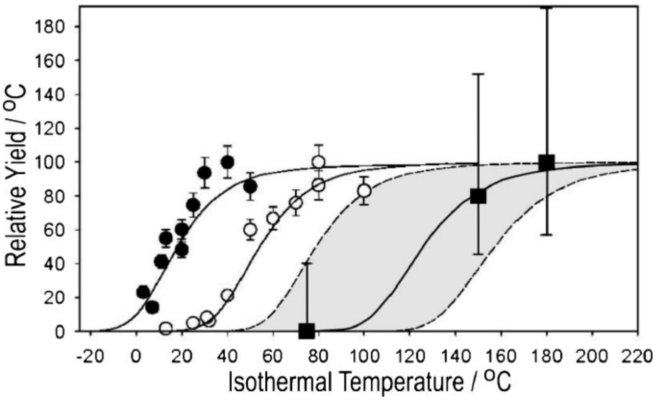

Fig. 8. Relative yields of $^{108}TcO_3Cl$ (full circles), $^{169}ReO_3Cl$ (open circles), and $^{267}BhO_3Cl$ (black squares) as a function of temperature. Error bars, including dashed lines, are 68% c.i. Solid lines are from Monte Carlo simulations with the standard adsorption enthalpies of −51 kJ/mol for TcO_3Cl, −61 kJ/mol for ReO_3Cl and −75 kJ/mol for BhO_3Cl. Adapted from [109].

This result shows that Bh behaves like a member of group 7 of the PTE and forms a volatile oxide chloride, presumably BhO_3Cl, which is less volatile than the compounds of the lighter homologs. The sequence of volatility is: $TcO_3Cl > ReO_3Cl > BhO_3Cl$. The deduced BhO_3Cl adsorption enthalpy of $-\Delta H_a^\circ = (75 + 9/-6)$ kJ/mol [109] is in excellent agreement with a theoretical prediction including relativistic effects [224]. This result coincides with the value expected from empirical correlations [225].

5.5 Hassium (Hs, element 108)

Hs is located in group 8 of the PTE. Like its lighter homologs Ru and Os, it is expected to show a property which is unique among all transition metals: formation of a highly volatile tetroxide MO_4 (M = Hs, Os, Ru) while exploiting the highest possible oxidation state (8+). All successful Hs chemistry experiments used HsO_4, explored its volatility [81] and reactivity [155], and exploited its volatility in nuclear synthesis and decay studies [78, 227] with unprecedented sensitivities. This gave access to new and interesting Hs isotopes – doubly-magic, deformed ^{270}Hs [72] and ^{271}Hs [80] formed in a 3*n*-evaporation channel – and their Sg and Rf daughter nuclides [78, 215]. In addition, these experiments confirmed the discovery of element 112 by measuring concordant decay properties in α-decay chains starting from chemically separated Hs fractions [78]. All these Hs isotopes were produced in reactions of ^{26}Mg on ^{248}Cm. A typical rate for the synthesis of 9.7-s ^{269}Hs, regularly used for chemical studies, was ≈ 3 atoms per day. More details about Hs chemistry experiments, including earlier, interesting but less successful attempts, are given in [25, 140].

The small step from Bh to Hs required a big leap in technological development to reach the speed and sensitivity required for chemical studies of isotopes with half-lives of seconds produced with cross sections of a few picobarn. The experimental set-up used in the first Hs chemistry experiment is schematically shown in Fig. 9. This experiment was unique, in a number of aspects: (i) A rotating wheel with ^{248}Cm targets [103] was applied for the first time in SHE chemistry to accept higher beam intensities. (ii) A chemical reaction with O_2 was performed "in-situ" in the recoil chamber named In situ Volatilization and On-line Detection (IVO) [81, 153]. A similar technique has been used earlier for lighter SHE in high-temperature TC [58, 96, 222]. In Hs experiments, this allowed a fast and highly efficient transport of chemically pre-separated HsO_4 to the detection system. (iii) While first experiments used COLD [81] and CTS [116] as low-temperature TC detectors, recent experiments were performed with COMPACT [123].

In the first experiment, seven nuclear decays of Hs isotopes were observed in a narrow peak [81] along the temperature gradient; see Fig. 10. From this observation, one concludes that a relatively stable, volatile HsO_4 is formed that has reached the detector. The adsorption position at (-44 ± 6) °C, in comparison with the one of OsO_4 at (-82 ± 7) °C, indicates a lower volatility – or, more precisely, a higher negative adsorption enthalpy – of HsO_4. This was theoretically not expected and it triggered elaborated theoretical work. Now, with the largest possible basis sets in a 4c-DCT calculation, very good agreement is achieved with

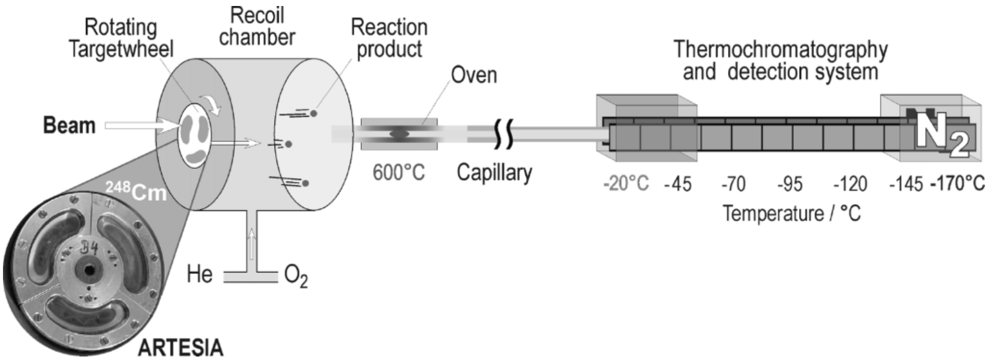

Fig. 9. Schematic view of the cryo-thermochromatography experiment and the rotating ^{248}Cm taget wheel (ARTESIA) used to investigate the HsO_4 volatility. Adapted from [81]. Original drawing courtesy of Ch. E. Düllmann.

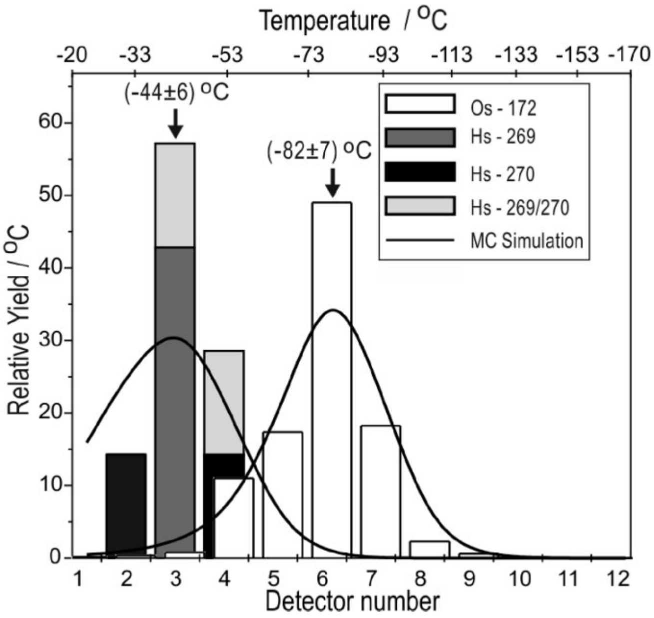

Fig. 10. Experimentally observed thermochromatogram of seven molecules of HsO_4 (filled histogram) and of OsO_4 (open histogram). Solid lines are results from Monte Carlo simulations. Adapted from [81]. Original drawing courtesy of Ch. E. Düllmann.

experimental results [228]. Experiments with Au and Al covered detectors in COMPACT confirmed the first findings, provided Hs data with better statistics, and showed that physisorption is the relevant adsorption process for HsO_4 [229]. These experiments were the first showing that SHE chemistry can be performed on a one-atom-per-day scale.

A different type of Hs experiment [155] was performed by a collaboration using a set-up dubbed CALLISTO. Also in this experiment, tetroxides were formed in-situ in a hot recoil chamber. Contrary to very dry gas conditions required for COLD and COMPACT, in this experiment H_2O vapor was added to the O_2 containing He. This gas mixture transported HsO_4 and simultaneously produced OsO_4 to a linear array of 12 detectors (PIN-diodes) facing a stainless steel plate coated with a thin film of NaOH. From the adsorption pattern of HsO_4 and OsO_4 at the beginning of the chemically reactive NaOH surface, presumably forming $Na_2[HsO_4(OH)_2]$ in analogy to the know osmate (VIII), it was concluded that HsO_4 and OsO_4 show a similar reactivity in this first acid-base reaction with HsO_4 [155]. This is in agreement with a theoretical calculation [230].

5.6 Meitnerium (Mt), darmstadtium (Ds), and roentgenium (Rg) – the 6*d*-elements 109–111

So far, no attempts have been made to investigate chemical properties of SHE located in group 9 to 11 of the PTE – meitnerium (Mt), darmstadtium (Ds) and roentgenium (Rg). In recent years, ^{48}Ca induced reactions with actinide targets provide means to access nuclides of these elements with half-lives in the 10-s range allowing chemical studies; see Fig. 2. But, picobarn cross sections make all studies very challenging. High-temperature TC tracer studies with their lighter homologs [231, 232] show that volatile oxides or hydroxides are good species for a chemical separation and characterization of Mt and Ds. In group 11, volatile $RgCl_3$ could be compared to $AuCl_3$. Theoretically, elements in group 11 are extensively studied because of their ability to form monovalent compounds; see the review of Pyykkö about Au [233]. Highly advanced relativistic coupled-cluster calculations [234] yield for the Rg atom a ground state of $6d^9\,7s^2$ – in contrast to its lighter homologs. Large relativistic effects are observed on orbital energies and level order for the Rg atom [234] and for the RgH molecule [235, 236]. Calculation of AuX and RgX (X=H, F, Cl, Br, O, Au, Rg, Li) show that the chemistry of Rg will be largely dominated by relativistic effects. A brief summary with recent references can be found in [84].

5.7 Copernicium (Cn, element 112)

Cn, located below Hg in group 12 of the PTE, is an especially fascinating element caused by its $6d^{10}\,7s^2$ closed shell configuration and a strong relativistic stabilization of the 7*s* orbitals. Very early on, the question how closely Cn would resemble the chemistry of Hg attracted much attention [43]. Relativistic calculations, which show a strong stabilization of the closed $7s^2$ shell, indicated the possibility that element 112 is rather inert – almost like a noble gas – and, in elementary form, a gas or a very volatile liquid (metal) [141]. Recent calculations [84, 237–239] (and [240] with somewhat different results) predict that a very volatile Cn would still retain a metallic character which would allow bond formation with metallic surfaces like Au [84, 239]. On inert surfaces, however, no adsorption is expected [84, 238]. Empirical extrapolations of sublimation enthalpies gave only 22 kJ/mol [241]. From empirical correlations, supported by adsorption data of Rn and Hg on metal surfaces [242, 243], an adsorption enthalpy range of -30 to -60 kJ/mol was predicted for Cn on Au – to be compared with about -29 and -98 kJ/mol for Rn and Hg, respectively [244].

First attempts to chemically study Cn [157, 243–245] tried the ^{48}Ca on ^{238}U reaction to synthesize ^{283}Cn. This isotope, as we know it today, predominantly shows α-decay with a half-life of 3.8 s and is produced with a cross section of about 2 pb [32, 35] or less [34]. Even if the authors published the observation of Cn, today, we must conclude that these early experiments did not convincingly identify ^{283}Cn, mostly because of false assumptions about decay properties ($T_{1/2} = 3$ min, SF) and assuming a too high cross section; all based on the knowledge of the early 2000s.

Technically most interesting and innovative were the first attempts made by Yakushev and coworkers [157, 245] at the FLNR in Dubna. To collect Cn from a gas stream, they used pairs of Au and Pd coated PIPS detectors at room temperature positioned inside an assembly of ^{3}He filled detectors to search for neutrons in coincidence with SF fragments [245]. In a second stage, this experiment added a flow-through ionization chamber behind the PIPS detector [157, 246]. Very advanced, but still not successful, were two low-temperature TC experiment by Gäggeler, Eichler and coworkers performed at the GSI with the IVO-COLD set-up [247, 248]. The Au-covered detectors had a temperature gradient from $+35\,^\circ$C to $-185\,^\circ$C. While the first experiment [247] was based on the false assumption of a 3-min ^{283}Cn with SF decay, the second experiment was adapted to the newly reported half-life of 3.8 s and to detect α-decay in almost 4π-geometry. However, even with a sensitivity limit of 2.5 pb reached, ^{283}Cn was not unambiguously detected [248]. Also, a follow-up experiment made at Dubna was not able to observe ^{283}Cn [40]; see [249] for a critical discussion of these experiments.

A break-through came at the FLNR when Eichler and coworkers [40, 41] used the reaction ^{48}Ca on ^{242}Pu to produce 0.48-s ^{287}114 with a cross section of 3.5 pb [32, 35]. The α-decay daughter ^{283}Cn was transported in a He/Ar gas mixture which was highly purified and circulated in a closed gas loop. Within about 2 s, products were transported to an improved COLD. In the first part of the experiment, it was operated at a temperature range from $-24\,^\circ$C to $-184\,^\circ$C and between $+35\,^\circ$C and $-180\,^\circ$C in the second part. A schematic view of the experimental set-up is shown in Fig. 11. Two α-decay chains assigned to ^{283}Cn were observed – one in the first part of the experiment (in detector 2) at $-28\,^\circ$C, directly in the deposition zone of simultaneously produced Hg, and one in the second part (in detector 7) at $-5\,^\circ$C; see panel (a) and (b) in Fig. 12. Because of a higher starting temperature and a shallower temperature gradient in the second experiment most of the Hg was deposited before detector 7 and only 5% of Hg reached this region. 65% of the simultaneously produced Rn was deposited on detectors 28 to 31 on the cold end of COLD and the rest passed through. From a Monte-Carlo simulation of the Cn adsorption on Au an enthalpy of $-(52+46/-7)$ kJ/mol (68% c.i.) was obtained. This indicates that Cn is sufficiently volatile for a “gaseous” transport (like Hg and Rn) to the detector.

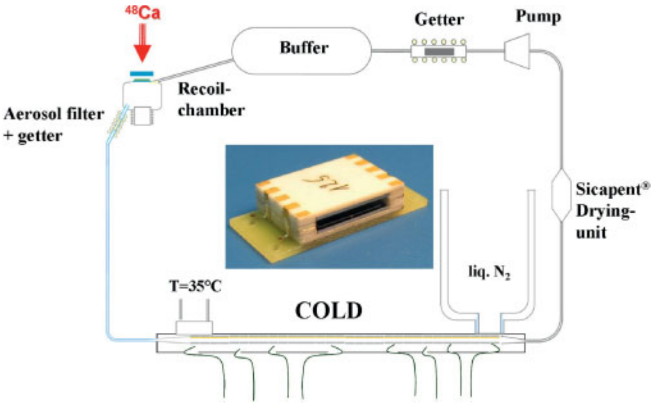

Fig. 11. Schematic view of the IVO-COLD device used in Cn and element 114 experiments at the FLNR in Dubna [41, 149, 249]. A highly purified He/Ar gas-mixture, circulating in a closed loop, transports products to a cooled array of 32 detector pairs (COLD); photo of one detector pair is shown. Figure adapted from [249]. Courtesy of R. Eichler.

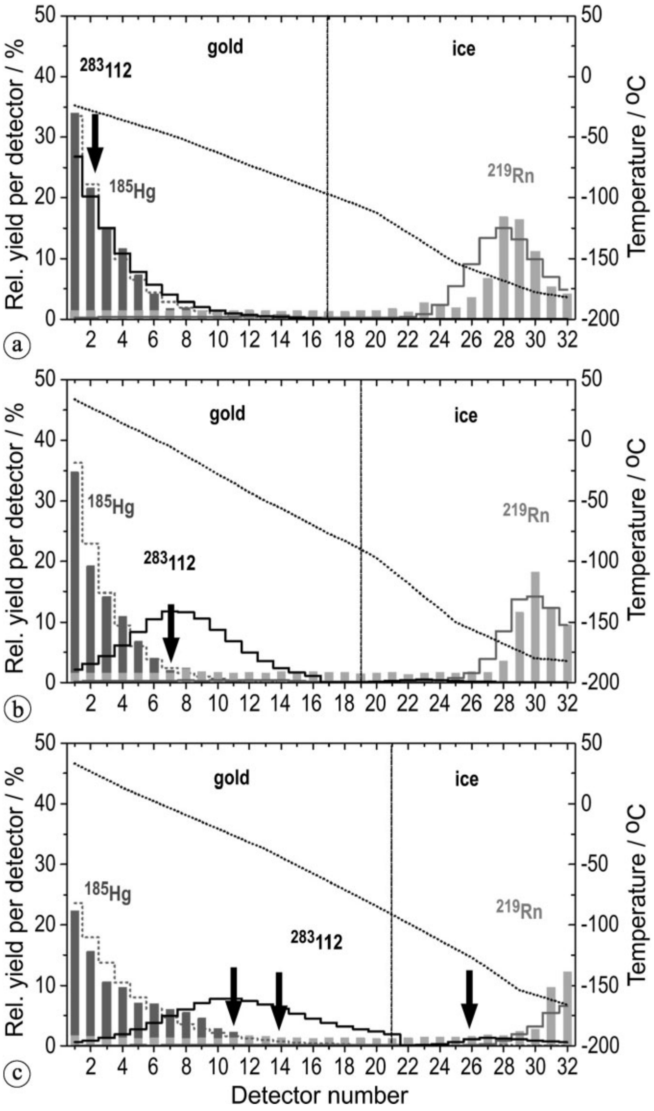

Fig. 12. TC deposition of ^{185}Hg (dark bars), ^{219}Rn (grey bars), and of ^{283}Cn (arrows, five events) in three experiments with the COLD. Results from Monte-Carlo simulations (dashed lines) and temperature distributions (dotted line, right-hand axis) are indicated together with regions for Au and ice covered detector. Figure adapted from [250]. Original drawing courtesy of R. Eichler.

In addition, contrary to Rn and more similar to Hg, Cn has a metallic character forming bonds with Au – typical for a group-12 element [40, 41]. This chemistry experiment was the first and independent confirmation of nuclear decay chains reported earlier from FLNR experiments about the synthesis of element $^{287}114$ and $^{291}116$ [32, 35]. A third experiment [250] was carried out with a higher gas-flow rate which yielded two atoms of ^{283}Cn deposited at $-29\,^\circ$C and $-39\,^\circ$C, respectively; see panel (c) in Fig. 12. One event was observed at a lower temperature ($-124\,^\circ$C) on the ice covered part of COLD. This measurement of one event in the low temperature region (in the tail of a distribution) does not contradict the other observation.

An analysis of this improved result reduced the error bar on the (unchanged) adsorption enthalpy of Cn on Au to $-(52^{+4}_{-3})$ kJ/mol (68% c.i.) [250]. This strongly supports the above mentioned conclusion about the high volatility of Cn and its metallic character expressed in a clear – but weaker than Hg – metal-metal bond formation with Au. All experimental findings [249], are in agreement with a fully-relativistic 4-c DFT calculation [84, 239]. Details on the discussion of extrapolated and theoretically calculated sublimation enthalpies can be found in [84, 239, 249, 250].

It is worthwhile noting that the above mentioned collaboration detected additional atoms of Cn during their element 114 studies [149, 249]; one ^{285}Cn atom was observed [129] after pre-separation with the DGFRS. The deposition temperature of one ^{285}Cn atom, observed in the course of element 114 studies at the GSI [149], was in good agreement with these earlier observations.

5.8 Elements 113 and 114

Element 113 marks the beginning of the $7p$ elements. Because of large (relativistic) spin-orbit effects on the $7p$ orbitals, these metals are expected to be more volatile than their lighter homologs in the sixth period of the PTE [84]. This trend also results from empirical correlations [241].

Nuclear physics experiments at the FLNR claimed the observation of isotopes of element 113 through the α-decay of element 115 and 117 parent nuclei synthesized in reactions of ^{48}Ca with ^{243}Am and ^{249}Bk, respectively [31, 32]. For element 113, a volatility between its lighter homolog Tl and element 114 is expected. The review of [249] reports about first, unpublished attempts at the FLNR to study the element 113 volatility. It is premature to draw any conclusion from these experiments. The formation of more volatile hydroxides would be an alternative approach in the gas phase chemistry of element 113.

Recently, Dubna–Livermore collaborations were credited with the discovery of element 114 and 116 [251] and, in the presently ongoing process, the proposed names and symbols flerovium, Fl, and livermorium, Lv, respectively, were provisionally recommended [252].

The volatility and reactivity of element 114 was in the focus of many theoretical calculations [43–49, 84, 239] and empirical extrapolations [241]. This is not only because element 114 was and often is considered the showcase SHE but also because of a strong relativistic stabilization of the $7p_{1/2}$ orbital which leads to a quasi-closed shell $7s^2\,7p^2_{1/2}$ ground state. From this, a high volatility and chemical inertness was inferred. Pitzer's question "Are elements 112, 114, and 118 relatively inert gases?" [141] remained a challenge for experimentalists for more than three decades.

The discovery of 0.48-s $^{287}114$, produced with a cross section of 3.5 pb in ^{242}Pu-based reactions [32, 35], and of 0.69-s $^{288}114$ and 2.1-s $^{289}114$, accessible with cross sections up to about 10 pb [37, 38] in ^{244}Pu-based reactions [32, 35], pushed the door open for chemical studies of element 114. Empirical extrapolations [241] and state-of-the-art relativistic theory [84, 238, 239] predict that element 114 is much more volatile than Pb but less volatile than Cn. It is also expected that element 114 is chemically more inert than Pb but still has a pronounced metallic character, *i.e.*, forms metal-metal bonds with Au. Thus, TC with Au covered detectors developed and applied for studies of HsO_4 and Cn were implemented in element 114 studies; partially adapted to an expected lower volatility of element 114.

Series of experiments were performed by Eichler and coworkers [149] at the FLNR with the IVO-COLD set up. The observation of one decay in the Cn experiments, which was assigned to $^{287}114$ and which was observed at the rather low temperature of $-88\,^\circ$C [149] ($-94\,^\circ$C given in [249]), came as a big surprise. It is not totally excluded, but rather astonishing, that an isotope with a half-life of 0.48 s was observed after a mean transport time of 2.2 s. If characteristic for element 114, this adsorption position would indicate less metallic (more inert) and more volatile properties than expected. Two additional events, assigned to $^{288}114$ and observed at deposition temperatures of $-4\,^\circ$C and $-90\,^\circ$C, were seen in subsequent experiments with ^{244}Pu as a target [149]. Because of a substantial background in the COLD directly coupled to a recoil chamber, the significance and assignment of at least some of these events to decays of element 114 was questioned [152]. But even if one accepts all nuclear decay assignments made in these experiments [149] one "chemical" problem remains. The deduced adsorption enthalpy of -34 kJ/mol for element 114 adsorbed on Au indicates a surprisingly high volatility – and would be in contradiction to fully-relativistic quantum theory which predicts a value of -69 kJ/mol [239]. However, a closer look at the error band ranging from -31 to -54 kJ/mol and -23 to -88 kJ/mol for a 68% and a 95% c.i., respectively [149], reveals that it just brackets the element 114 behavior between Hg and Rn. Also the way how this error band was determined and how far it extends into a high temperature region (not covered by the COLD) is not free of criticism [152]. Thus, no final conclusion on a metal-like character of element 114 and its volatility in comparison with element 112 can be drawn from these, without any doubts, pioneering experiments on element 114.

The element 114 chemistry experiment by Yakushev and coworkers [123] at the GSI circumvented two major problems of the previously described experiment. By using TASCA [110, 121] as a pre-separator [112, 152], the nuclear decay background from unwanted products was drastically reduced and became negligible. Coupling two COMPACT detectors in a row and operating the first one (isothermal) at room temperature allowed a much better resolution at higher temperatures. This is especially relevant to find differences in adsorption temperatures of some of the less volatile elements. From this experiment, a publication about a comparison of element 114 with Pb, Hg, and Rn is in preparation. Pershina and coworkers predict that element 114 should form metallic bonds and adsorb on Au much weaker than Pb, stronger than Cn, and about the same as Hg [239]. Consequently, element 114 is expected to appear at the beginning of the chromatography column at about the position of Hg. The calculated trend in binding energies of atoms adsorbed on a Au surface is Pb $\gg$ 114 > Hg > 112 > Rn. Taking into account that Hg usually dissolves into the Au lattice, which results in an energy gain of about 29 kJ/mol, an experimentally observable adsorption sequence of Pb $\gg$ Hg > 114 > 112 > Rn is theoretically predicted [84].

No direct attempts have been made to chemically study elements beyond element 114. However, techniques have been developed to make use of neutron-rich, long-lived isotopes of lower-Z superheavy elements produced in α-decay chains of, *e.g.*, element 115 [253].

The longest lived isotopes of element 115 have half-lives in the 200-ms range: ^{288}115 produced with a cross section of about 3 pb in reactions with ^{243}Am [32] and ^{289}115 as the α-decay daughter nucleus from ^{293}117 synthesized with a about 1 pb in reactions with ^{249}Bk [31]. These isotopes may allow access to chemistry of element 115 in the future.

6. New developments and perspectives

6.1 Chemistry after physical preseparation

The formidable progress in SHE chemistry over the last decades – from first studies of Db to recent investigations of element 114 – was only possible and closely related to enormous technical developments along the entire chain of synthesis, transport, separation, and detection of SHE. It was not only the continuous improvement of speed, efficiency, and automation of devices and techniques which enabled this progress, but also the implementation of novel instruments and coupling of hitherto separate set-ups. One of the most recent and most promising developments, opening completely new perspectives, is the coupling of chemistry devices to physical pre-separators; so far, always gas-filled recoil separators. This technique was pioneered at the BGS in Berkeley and is now established at all major SHE research laboratories. An overview can be found in [112]; see Sect. 4 for more details and references. As already mentioned, enormous advantages arise from (i) the background reduction after unwanted nuclear reaction by-products are already separated in flight and (ii) the absence of any "destructive" primary beam passing though the recoil transfer chamber. A few aspects and potential future applications will briefly be mention in the following.

6.1.1 Gas phase chemistry

Coupling gas-phase chemistry devices to recoil separators, *e.g.*, COMPACT to TASCA, make on-line measurements and identification of short-lived nuclei at a rate of one-atom-per-day or even week only possible because of an unprecedented low background. The element 114 experiment at the GSI [123] is a prime example for this development which will be of importance for future experiments in this region. Especially for studies of 7p elements, a pre-separation of their lighter 6p homologs is essential because of an otherwise strongly interfering background from their α-decay. Further studies of element 114, urgently required to clarify open questions, and of element 113 and 115 will profit from the use of a pre-separator.

In the past, test experiments and developments towards vacuum chromatographic techniques were made [241]. This has the potential of very fast separations well below the one second range. However, considerable development is still required towards a new type of RTC with a (very) hot catcher for sufficiently fast release times.

Most exciting is a new development which opens up the new and very appealing class of metal-organic compounds for SHE. They become accessible because of the absence of primary beam in an RTC. First tests in this direction were performed with hfa-complexes at the BGS [120]. Recently, exploratory experiments performed at the Mainz TRIGA reactor with 4d elements and at the TASCA with 5d elements show, that, in a first step towards metal-organic compounds, carbonyls are accessible one-atom-at-a-time for a wide range of elements [131]. Plans are under way to perform a ground breaking gas-phase chemistry experiment on the formation, stability, volatility, and detection of $Sg(CO)_6$ in a large international collaboration. At the GARIS recoil separator of RIKEN, Haba and coworkers [117, 124, 125] have successfully synthesized and pre-separated the isotope ^{265}Sg which is available at a rate of about one atom per hour for chemical investigations [79]. This gave access to detailed nuclear decay studies of the ground-state and the isomeric state of ^{265}Sg [79] and to the complex decay pattern into two states of ^{261}Rf [126, 127]. These experiments confirmed results from an earlier meta-analysis [215]. If successful, the $Sg(CO)_6$ experiment will open the new field of metal-organic chemistry of SHE. This will allow for a completely new approach not only to explore chemical properties of these compounds but also to test fully-relativistic theoretical models in a chemically uncharted region of SHE at the limits of existence of our nature.

6.1.2 Liquid phase chemistry

Continuous and very fast chemical separations of Rf with SISAK coupled to the BGS were the first aqueous-phase chemistry experiments exploiting pre-separation [113, 119, 139]. As nuclides with half-lives down into the one second range are accessible with high yield and high detection efficiency in an automated process, this technique has the potential to be extended far into the region of heavier SHE. Presently, developments are underway in a Norwegian-Japanese collaboration to prepare an aqueous-phase chemistry experiment with Sg and, if promising, to carry out the first redox reaction of a SHE. Expertise gained in redox reactions with No [254] will be of substantial help in this preparation. Such a study would be most interesting as it allows a direct comparison with theoretically predicted redox potentials [255]. The SISAK technique may very well be suitable to extend aqueous-phase studies to elements beyond Sg. In the preparation of a Hs experiment [256], a test was successfully performed [257] with SISAK coupled to the TASCA. Therefore, it can be anticipated that this techniques will not only give access to more detailed chemical studies of Sg but can open up new frontiers in the aqueous chemistry of SHE. Conceptually, not only the (in liquid the phase) "missing" elements Bh and Hs but also heavier elements – even up to element 114 – should be accessible to liquid-phase chemistry in the future.

Presently still in its infancy, continuously working liquid-liquid extractions systems in microchip devices [258, 259] may also play an important role in these studies. Among others, interfacing problems with transport systems and detectors need to be tackled. One advantage of such devices would certainly be the very small consumption of chemicals on the microliter scale. Very small volumes may also ease the coupling of streams of liquids to detection systems.

In a proof-of-principle experiment, separating ^{261}Rf in ARCA II coupled to TASCA, it was shown that also automated, batch-wise liquid chromatographic separations can be performed in such a combination [260]. Column chromatographic separations have the disadvantage of being slower and very demanding in automation but they offer a much wider selection of chemical systems to be tested; however, only if isotopes with sufficiently long half-lives are available. The need for pre-separation was demonstrated at TASCA while testing devices and procedures for a batch-wise electrochemical reduction of Hs [118]. The on-line produced ^{175,177}Os tracer activity was only visible in the γ-spectrum after pre-separation. As challenging as it is, an electrochemical reduction of Hs(VIII) in aqueous solution would be a very interesting experiment.

6.2 Conclusion

All chemical studies justify positioning of the transactinides – or superheavy elements –, beginning with element 104, into the seventh period of the Periodic Table. Chemical studies on their behavior in the aqueous phase have extensively been performed with Rf and Db and first insights into Sg properties have been obtained. Studies in the gas phase have been carried out for Rf, Db, Sg, Bh, Hs, and Cn – and have now reached element 114.

All experimental results yield properties which, in general, place these elements into their respective group of the PTE: Rf, Db, Sg, Bh, Hs, and Cn into group 4, 5, 6, 7, 8, and 12, respectively. This demonstrates that the Periodic Table remains an appropriate ordering scheme also regarding the chemical properties of these elements. However, a closer look reveals that some properties are no longer reliably predictable by simple extrapolations in the Periodic Table.

Even if sometimes an “oddly ordinary” [261] behavior is found, this cannot be taken as evidence that other SHE will behave as extrapolated. Sometimes relativistic effects and other effects, like shell effects, may just cancel to “mimic” a normal behavior. However, fully-relativistic calculations provide data which often allow for a quantitative comparison with experimental results. Excellent agreement was demonstrated in a number of cases. From this, one can deduce that relativistic effects strongly influence the chemical properties of SHE. Elements 112 (Cn) and 114, presently the hottest topic in this field, are the ones with the most pronounced relativistic effect. It will be most interesting to see, which detailed chemical properties of these elements can be unraveled. In combination with modern fully-relativistic atomic and molecular calculations, SHE provide the crucial test-bench for relativistic effects in chemistry.

In addition to element 114, fascinating and challenging prospects are ahead including the path into metal-organic chemistry. More detailed information on the aqueous phase chemistry of Sg and heavier elements will be accessible through continuous on-line separations. The region between element 108 and 112 is waiting to be “chemically” discovered. First attempts for a study of element 113 have been made and element 115 may become accessible in sub-second gas phase or vacuum chromatography.

Coupling of chemical separation set-ups to physical recoil separators provides a big leap into a completely new quality of SHE chemistry. In addition to fascinating chemistry aspects, these experiments will certainly provide multifaceted nuclear data and they are vital tools for a clear identification of the atomic number of superheavy elements.

To become successful, all these efforts to push the frontier in SHE chemistry towards its limits will not only need close cooperation between nuclear chemistry groups at universities and large scale research laboratories but require strong international collaborations to meet all challenges of such enterprises.

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