Chemistry of the superheavy elements

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The quest for superheavy elements (SHEs) is driven by the desire to find and explore one of the extreme limits of existence of matter. These elements exist solely due to their nuclear shell stabilization. All 15 presently ‘known’ SHEs (11 are officially ‘discovered’ and named) up to element 118 are short-lived and are man-made atom-at-a-time in heavy ion induced nuclear reactions. They are identical to the transactinide elements located in the seventh period of the periodic table beginning with rutherfordium (element 104), dubnium (element 105) and seaborgium (element 106) in groups 4, 5 and 6, respectively. Their chemical properties are often surprising and unexpected from simple extrapolations. After hassium (element 108), chemistry has now reached copernicium (element 112) and flerovium (element 114). For the later ones, the focus is on questions of their metallic or possibly noble gas-like character originating from interplay of most pronounced relativistic effects and electron-shell effects. SHEs provide unique opportunities to get insights into the influence of strong relativistic effects on the atomic electrons and to probe ‘relativistically’ influenced chemical properties and the architecture of the periodic table at its farthest reach. In addition, they establish a test bench to challenge the validity and predictive power of modern fully relativistic quantum chemical models.

1. Introduction

Chemical elements are basic building blocks of matter. Over the past century, deep knowledge has been gained about the inner structure and properties of the atomic nucleus and the electronic structure, which determines all chemical properties. The chemistry of superheavy
elements (SHEs) [1] provides a crucial and challenging testing ground to advance our understanding of the properties of matter at its limits of existence.

Advancing hand in hand, today, experimental and theoretical achievements allow not only to put these elements into their place in the periodic table of the elements (PTE) but also to contribute to the advancement of the PTE from basic ones, like Mendeleev’s seminal table [2], via Seaborg’s introduction of the series of actinides [3] to the more recent and most advanced ones based on relativistic calculations. In the freedom theoreticians have to expand concepts far beyond our experimental reaches and driven by the quest to establish the ultimate form of the PTE, it is expanded all the way up to elements 172 and 173 [4–6]. At this atomic number, the 1s electrons reach such a high speed that the binding energy, increased by the relativistic effect, reaches $2m_e c^2$ ($m_e$ is the electron rest mass and $c$ the speed of light) and the electron ‘dives’ into the negative-energy continuum. Currently theory has no instruments to treat such systems in quantum electrodynamics comprehensively and, therefore, this defines today’s limit of the theoretical description of electron configuration [6]. Modern, fully relativistic theories [7] are essential tools to overcome simple, sometimes misleading, empirical extrapolations to predict or explain properties of a SHE, i.e. all elements with atomic number higher than 103. These are also often termed transactinide elements.

As these chemistry experiments are strongly intertwined with nuclear physics aspects through the nuclear synthesis and the decay of the heaviest nuclides, they provide insights into nuclear aspects which complement nuclear physics experiments. However, with all the great success made over the last decades, what remains until now are several questions about the ultimate limit of matter and of the existence of chemical elements; e.g. How many can exist from a nuclear and from an atomic perspective? How many can there be in our Universe or can be synthesized on the Earth? What nuclear, atomic and chemical properties do these elements have? These questions are driving the quest for SHEs.

During the past half-century, discoveries of 15 new chemical elements have been reported. They are all transactinides or SHEs. Today’s PTE comprises 118 chemical elements of which 114 have been accepted and named by the International Union of Pure and Applied Chemistry (IUPAC). A brief overview over this historical development, nuclear synthesis and decay aspects and the rationale to term elements with atomic number larger than 103 SHEs is given in §2.

After introducing nuclear aspects, this article briefly discusses relativistic effects and the structure of the PTE in §3. In §4, it outlines in an illustrative way experimental results and advanced techniques applied to determine atom-at-a-time chemical properties of rutherfordium (Rf, element 104) compounds in the liquid phase, of seaborgium (Sg, element 106) compounds in the liquid phase and gas phase and of hassium (Hs, element 108) tetroxide in the gas phase. At the end, wall-adsorption experiments of atoms of copernicium (Cn, element 112) and flerovium (Fl, element 114) from the gas phase are outlined which probe the influence of the pronounced relativistic stabilization of the $s$ and $p_{1/2}$ orbitals. Because of the large spin–orbit splitting, not only the filled $s$ orbital but also the $p_{1/2}$ can be regarded as a closed shell. Reviews on the experimental results of SHE chemistry experiments, including dubnium (Db, element 105) and bohrium (Bh, element 107), which are not discussed here, can be found in [8–12] and in the most recent and comprehensive work of Schädel & Shaughnessy [1].

2. Nuclear aspects

(a) The region of superheavy elements

In the year 1961, the search for the first transactinide element with atomic number 104 had begun when the new heavy ion cyclotron U300 went into operation at Dubna. Worldwide, new technological developments and the newly arriving computers greatly contributed to the advancement of science. In 1966, a conference at Lysekil and the publication of several seminal articles gave the starting signal for the rush into the new era to search for, discover and investigate
SHEs. While early and more qualitative work had made it conceivable that SHEs may exist around atomic number \( Z = 126 \), these new results focused on the existence of an ‘island of stability’ centred at \( Z = 114 \) and neutron number \( N = 184 \). These early developments are outlined in [13].

Today, discoveries of 15 transactinides with about 100 new nuclides have been claimed filling the PTE up to element 118. After the acceptance of the discovery of elements 114 (flerovium, Fl) and 116 (livermorium, Lv) [14,15], the official acceptance of the discovery of elements 113, 115, 117 and 118 is pending. While more details about nuclear synthesis paths and decay properties will be given in the next section, in the following, we will discuss what a SHE is from a nuclear perspective.

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’ [13]. Up to that time, and typical for closed-shell nuclei, SHEs were expected to have a spherical shape. However, in 1984 the discovery of element 108 [16] led to a different opinion. New experimental results [17] and theoretical concepts, which take into account shell-stabilized deformed nuclei and emphasize the importance of the newly discovered \( N = 162 \) neutron shell, show that there is no ‘island of stability’ in a ‘sea of instability’ [18]. Instead, there is a region of shell-stabilized, deformed superheavy nuclei with enhanced stability against spontaneous fission (SF) centred at the doubly magic nucleus \( ^{270}_{108}\text{Hs}_{162} \) [19]. 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. Theories indicate that nuclei with atomic number 120 and 126 are candidates for the next closed shell; with a possibility of even more pronounced shell stabilization than in element 114. In contrast to rather localized shells in lighter elements, extended regions of shell-stabilized nuclei appear in SHEs [20].

The definition of SHE varied over time and among different groups of people. Today, there is a consensus among many scientists that SHEs begin with element 104 [12,20,21]. For chemists, this is especially appealing in as much as the beginning of SHEs coincides with the beginning of the transactinides. Two assumptions are used for this definition. Firstly, SHEs owe their stability, i.e. their existence, solely to 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. Theoretically calculated half-lives for SF—without extra (nuclear) shell stabilization—fall below the \( 10^{-14} \) s mark for elements 104 and higher [12,20]. The factors of up to \( 10^{17} \) longer measured half-lives for Rf isotopes exhibit the influence of shell stabilization. From this, one can claim that all elements beginning with Rf live only because of their microscopic shell stabilization and, therefore, shall be called SHEs.

(b) Nuclear syntheses and decays

Elements beyond fermium are produced at accelerators in nuclear fusion reactions with charged particles; heavy ions are needed to reach SHEs. Depending on the target–projectile combination, which can result in significantly different excitation energy of the compound nucleus, they can be classified as ‘cold fusion’ and ‘hot fusion’ reactions [22]; sometimes also the term ‘warm fusion’ is used to characterize the intermediate situation typical for the below-mentioned reactions with \( ^{48}\text{Ca} \) beams. After the discovery of elements up to Sg in hot fusion reactions, which involve actinide targets and light ion beams, elements 107–112 were first synthesized in cold fusion reactions, which use Pb and Bi targets and medium heavy beams [17]. The synthesis of element 113 in the \( ^{70}\text{Zn} \) on \( ^{209}\text{Bi} \) reaction [23] was extraordinarily difficult. It may mark the end of the cold fusion path. Cold fusion reactions lead to neutron-deficient, relatively short-lived nuclei of SHE which are of very limited use for chemical studies [9,12,22].

Over the last decade, hot fusion experiments were carried out at the Flerov Laboratory of Nuclear Research (FLNR) in Dubna irradiating targets from \( ^{238}\text{U} \) to \( ^{249}\text{Cf} \) with \( ^{48}\text{Ca} \) beams. Products were separated with the Dubna gas-filled recoil separator. These experiments provided a breakthrough and led to reports about the discovery of elements up to 118 [24]. An experiment with GSI’s gas-filled separator, the TransActinide Separator and Chemistry Apparatus (TASCA),
using a $^{244}$Pu target confirmed the synthesis of the two most neutron-rich isotopes of element 114, 0.69-s $^{288}$Fl and 2.1-s $^{289}$Fl [25]. Moreover, it showed that these two isotopes are produced with a cross section of the order of 10 pb [25,26]—the highest cross section observed in $^{48}$Ca-induced production of transactinides. Under optimized conditions, this may lead to production rates of up to about 10 Fl atoms per day. All nuclei that are produced in $^{48}$Ca-induced reactions have longer half-lives and are produced with higher cross sections than the ones made in cold fusion reactions. This provides great perspectives for chemical studies. In contrast to the discovery of elements 107–112, these experiments suffer a disadvantage that their nuclear decay is not ‘genetically’ linked by unequivocal $\alpha$-$\alpha$-decay sequences to the region of known nuclei—a prerequisite used for unique identifications [17]. Recently, an experiment at TASCA paved the way for future unique identifications of the atomic number through characteristic K-X rays [27].

Frequently used reactions for the production of nuclides applied in chemistry experiments from element 104 to 108 are $^{248}$Cm($^{18}$O,5n)$^{261}$Rf, $^{249}$Bk($^{18}$O,5n)$^{262}$Db, $^{248}$Cm($^{22}$Ne,5n)$^{265}$a,bSg, $^{249}$Bk($^{22}$Ne,5n)$^{267}$Bh and $^{248}$Cm($^{26}$Mg,4–5n)$^{269,270}$Hs [22]. In these experiments, typical intensities range from 2 to $6 \times 10^{12}$ s$^{-1}$ ions impinging on thin target films with thicknesses usually between 0.3 and 1 mg cm$^{-2}$. As cross sections drop from about 10 000 pb to less than 10 pb from Rf to Hs, respectively, production rates decrease from about 4 min$^{-1}$ for 68-s $^{261}$Rf, 2 min$^{-1}$ for 34-s $^{262}$Db, 5 h$^{-1}$ combined for 14-s and 9-s $^{265}$a,bSg (two half-lives indicate the presence of an isomeric state in addition to the ground state) and 1 h$^{-1}$ for 17-s $^{265}$Bh to 2 d$^{-1}$ for 10-s $^{269}$Hs [12,22]. Taking into account, collection and transport efficiencies including nuclear decay losses, between 10% and 80% of these short-lived nuclei become available for chemical investigations; for more details, see [9] and §4.

In recent years, the first successful chemistry experiments were performed with Cn [28–30] and Fl [31,32]. Hot fusion reactions with targets of $^{242}$Pu and $^{244}$Pu and beams of $^{48}$Ca provided access to 0.5-s $^{267}$Fl, 0.69-s $^{288}$Fl and 2.1-s $^{289}$Fl. These longest-lived Fl isotopes are useful for chemistry. Note that due to limited statistics all the given Fl half-lives are associated with large error bars. So far, the observation of directly produced 3.8-s $^{283}$Cn synthesized in the reaction of $^{48}$Ca with $^{238}$U [24] has not been successful in chemistry experiments. However, $^{283}$Cn became accessible as the daughter nucleus from the $\alpha$-decay of $^{287}$Fl. Depending on details of a given experiment, i.e. selection of a specific nuclear reaction and the selected isotope, target thickness and beam intensity, typical production rates varied roughly between 0.5 and 5 atoms per day. As mentioned earlier, only a fraction becomes available for chemical studies. All these data clearly show that SHE chemistry is always performed ‘atom-at-a-time’ with single atoms or ions.

Chemistry can be a tool in elemental identification. To that end, chemical experiments have to demonstrate, often together with characteristic nuclear decay properties, unique chemical properties of a new element under investigation excluding any other chemical element. A step into this direction was made by experiments with Cn [28,29]. It provided the first independent confirmation of reports about syntheses of Cn.

Presently, no answer can be given to the question about the limit of existence of chemical elements from a nuclear structure perspective, i.e. what is the heaviest atomic nucleus which lives at least $10^{-14}$ s, and from a nuclear reaction point of view, i.e. what is the heaviest nuclear system which can be formed into a chemical element. These are most ambitious questions and theoreticians are striving to shed light on these presently still open issues.

3. The periodic table and relativistic effects

The PTE (figure 1) is the basic ordering scheme for chemical elements and an important tool in predicting chemical properties. The atomic number and the associated electronic configuration of an element define its position in the PTE. Trends in chemical properties are linked to trends in electronic configurations along groups or periods. But will this correlation break down at the far—or maybe even not so far—reaches of the PTE? What is the architecture of the PTE for the heaviest elements, where will the PTE end and how do we define or determine this end? How strongly does the position of a SHE in the PTE correlate with its chemical property? Such a loss
of correlation, which we have not reached yet, can be seen as the end of a ‘predictive’ PTE. In addition, there is also the possibility that the periodicity of the PTE in itself is lost, which may happen in the eighth period in the super-actinides beyond element 120 [5]. Theoreticians have been addressing these questions for more than 40 years [4–7]. The key ingredient is the relativistic treatment of the electrons and the use of an extended atomic nucleus. Relativistic theories provide input for a well-structured PTE up to elements 172 and 173 [4–6], where also theory is entering a very challenging ‘terra incognita’. Whether element 173 marks the end of the PTE and defines the limit of existence of chemical elements from an atomic perspective or whether this is the present limit set by constraints in theoretical modelling must remain open for the moment.

Already for the early transactinide elements, calculations show a large influence of relativistic effects on the energetic position and the sequence of electrons in their respective orbitals. This is associated with changes in their radial distributions. These changes are so pronounced that significantly different chemical properties than anticipated from empirical extrapolations in the PTE can be expected. Thus, experimental studies, in addition to unravel these properties, provide a test bench to validate modern relativistic calculations and probe their predictive power towards the heaviest yet unknown elements. In a synergistic interaction, calculations provide data for a better understanding of experimentally observed properties. 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, allow detailed predictions of chemical properties of SHEs. Reviews of theoretical work including predictions of chemical properties can be found in [7,33–36].

In analogy with the sixth-period transition elements following after group 3, SHEs occupy the seventh period of the PTE. They form a new series of 6d-transition elements followed by the 7p elements 113–118 [7]. In general, at least for the beginning of SHEs, chemical properties similar to those known from lighter transition metals in the fifth and sixth period can be anticipated. First-generation experiments with Rf [37–39], Db [40,41], Sg [42], Bh [43] and Hs [44] rendered sufficient justification to place these elements into group 4, 5, 6, 7 and 8, respectively. However, as seen in several detailed investigations, it is by no means trivial to assume that transactinides will exhibit
chemical properties, which can in detail be deduced from their position in the PTE. Relativistic effects become increasingly strong and, in interplay with shell effects, significantly influence the behaviour of these elements. The aspect of ‘relativity and the periodic system of elements’ has been in the focus since decades [4,33,45].

Relativistic effects in SHEs are discussed in [7,33–36]. The relativistic mass of the electron, \( m \), is \( m = m_0 / [1 - (v/c)^2]^{1/2} \), where \( m_0 \) is the electron rest mass, \( v \) is the velocity of the electron and \( c \) the speed of light. While the \( m/m_0 \) ratio is 1.000027 for H it exceeds 10% from the sixth period onward and reaches values of 1.79 for Fl and 1.95 for element 118 [7]. The effective Bohr radius (in Gaussian units) \( a_B = a_B^0 [1 - (v/c)^2]^{1/2} \) decreases with increasing electron velocity. This orbital contraction and stabilization of the spherical \( s \) and \( p_{1/2} \) electrons is the direct relativistic effect. Originally, it was 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 SHEs. Thus, the 7\( s \) orbital of element 112 is relativistically stabilized by 5.8 eV, i.e. doubling the binding energy when compared with the non-relativistic case, and it is 25% contracted [7].

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. For example, for element 106 even the level sequence of \( s \) and \( d \) orbitals is inverted. In contrast to its lighter homologues in groups 6 the 7\( s \) orbital in Sg is energetically below the 6\( d_{5/2} \) and 6\( d_{3/2} \) ones. It can easily be anticipated that this may lead to unexpected oxidation states, ionic radii different from those expected from simple extrapolations or changes in the ionic and the covalent part 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 in size compared with typical bond energies. The SO splitting of the valence 7\( p \) electrons in element 118 may be as large as 11.8 eV [7]. 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 is why it is most fascinating to experimentally probe the highest \( Z \) elements.

4. Chemical aspects

Since the beginning of chemical studies of the transactinides about half a century ago, our knowledge of chemical properties of SHEs has advanced enormously because of technical developments of automated rapid chemistry and detection techniques and modern, fully relativistic theories. Today, chemical information can be obtained from one atom per day or even week with nuclides that live about 1 s or more. The wealth of information available on SHE chemistry goes far beyond the scope of this article. In an illustrative way, some typical and remarkable aspects of SHE chemistry, together with the techniques applied [46], are discussed here.

In the aqueous-phase hydrolysis, complex formation and the stability of oxidation states are of importance. Rf and Sg are selected to exemplify techniques and to show similarities and deviations of chemical properties. More information on the aqueous-phase chemistry of Rf, Db and Sg, the heaviest element which has been studied in a liquid phase up to now, can be found in [9,10,12,47].

The in situ formation of a volatile compound and its deposition along a negative temperature gradient in a cryo-thermochromatography (c-TC) detector will be shown for group-8 element Hs, the heaviest element on which the formation of a chemical compound and its behaviour has been studied so far. More information on the gas-phase chemistry of Rf, Db, Sg and Bh can be found
in [8,11,48,49]. Thermochemical data of lighter elements and their application to studies of the heaviest elements are discussed in [50].

Currently the most exciting topics in SHE chemistry are the volatility and metallic character of Cn and Fl. Here, most pronounced relativistic effects, acting in combination with electron-shell effects, are expected. The present status of theoretical predictions and adsorption studies on Au will be discussed for atoms of Cn and Fl.

Before discussing chemical properties of SHEs, it is appropriate to emphasize the specific and ultimate character of chemical investigations with single short-lived atoms; often termed single ‘atom-at-a-time’ chemistry [51]. Kinetic and thermodynamic aspects, boundary conditions for the proportionality between the law of mass action (for macro amounts) and probabilities of finding an atom in one species or another (for single atoms) and a comparison between static and dynamic partition experiments is addressed in [51].

One atom-at-a-time chemical separations of short-lived isotopes require stringent optimization of all steps from (i) the selection of the nuclear reaction and the selection of the isotope, (ii) the techniques to bring highest intensity heavy ion beams on chemically, mechanically and thermally most stable targets, (iii) the collection and transportation efficiency from a collection (‘recoil’) chamber to a chemical apparatus, (iv) speed of this transport, usually in a flowing gas, and speed of the chemical separation process, (v) selectivity of the process and significance of the chemical result, (vi) sample preparation and the entire arrangement of detector(s) and data acquisition and (vii) purity (signal-to-noise ratio) of the measured sample. It is a great challenge, but it can also be very attractive and interesting, to master these tasks across all different scientific and technical disciplines [8–12,46].

(a) Rutherfordium (Rf, element 104)

Pioneering experiments showed that Rf has properties in agreement with its position in group 4 of the PTE [37–39]. Detailed recent studies, however, revealed a number of surprises [8–12,47–49]. In the following, liquid-phase fluoride complexation experiments will be sketched to demonstrate pronounced differences between Rf and its lighter homologues zirconium (Zr) and hafnium (Hf).

Studies in the aqueous phase aim at unravelling the competing strength of hydrolysis and complex formation with halide anions. To compare and understand measured distribution coefficients (K_d), theoretical model calculations [7,52] were applied to calculated hydrolysis constants and complex formation constants for group-4 elements [9,10,12,53]. Theory predicts for cation-exchange separations in dilute (less than 10^{-2} M) HF a K_d-value sequence of Zr ≥ Hf > Rf. This reflects the decreasing trend Zr ≥ Hf > Rf in the formation of positively charged complexes. The successive F^- complex formation of cationic species of Zr, Hf, Th and Rf was studied in mixed 0.1 M HNO_3/HF solutions [54] with the Automated Rapid Chemistry Apparatus (ARCA) [55]. For Zr and Hf, K_d-values drop between 10^{-4} and 10^{-2} M HF. Rf shows this at about 1 order of magnitude higher HF concentrations. This establishes the following sequence of F^- complex formation strength at low HF concentrations: Zr ≥ Hf > Rf. Confirming data were obtained with the automated ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [53,56,57]. It was found that the species MF_3^+/MF_2^{2+} are present for Rf and its homologues. The observed sequence of extraction and complex formation is in agreement with theoretical expectations [52].

Studies of anionic species in mixed HF/HNO_3 solutions, performed on an anion-exchange resin, yielded a surprise [54]: while from 10^{-3} to 10^{-1} M HF K_d values for Zr and Hf increase from ≈10 to above 100 no significant rise was seen for Rf. However, follow-up experiments showed for Hf a significant and for Rf an even more pronounced dependence of the adsorption probability on NO_3^- and HF_2^- counter-ion concentrations [9,47,53].

The formation and adsorption of MF_6^{2-} complexes of Zr, Hf and Rf was studied in detail with AIDA from 0.0005 to 0.013 M of equilibrated [F^-], taking into account the influence of NO_3^- and HF_2^- counter ions [58]. While RF_6^{2-} was formed, its formation constant, however, was at least one order of magnitude smaller than those of ZrF_6^{2-} and HfF_6^{2-}. In qualitative agreement with
(b) Seaborgium (Sg, element 106)

Seaborgium chemistry experiments in the aqueous phase and in the gas phase were carried out at the GSI, Darmstadt, \([42,59–62]\) by using \(^{265}\)Sg synthesized in the \(^{22}\)Ne + \(^{248}\)Cm reaction. Today we know that \(^{265}\)Sg \([63]\) has two states with half-lives of about 9 and 16 s, respectively. From its position in group 6 of the PTE, Sg is expected to behave similarly to Cr, Mo and W. Oxides, oxide halides and hydroxide halides are important and characteristic compounds of these elements. The formation and properties of such Sg compounds have been investigated in the aqueous phase and in the gas phase; most recently complemented by studies of the carbonyls.

(i) Liquid-phase chemistry

As discussed for group-4 elements, hydrolysis and complex formation are also central aspects in Sg studies performed in the aqueous phase \([42,59,60]\) on cation-exchange resins in ARCA II \([55]\). In the first experiment, performed in 0.1 M HNO\(_3\)/5 \(\times\) \(10^{-4}\) M HF, three \(^{265}\)Sg daughter nuclei were detected. From this, it was concluded \([42,59]\) that (i) Sg elutes together with Mo and W, (ii) it behaves like a typical group-6 element and forms hexavalent ions, (iii) it forms neutral or anionic oxide or oxide halide compounds, and (iv) it does not form seaborgyl ions (SgO\(_2\)\(^{2+}\))—different
from its pseudo-homologue U. By analogy with Mo and W, it can be assumed that Sg is forming a (hydrated) anionic complex like SgO$_2$F$_3$\(^-\) or the neutral species SgO$_2$F$_2$. Such properties are typical for group-6 elements—but not for U.

As the formation of seaborgate ions (SgO$_4^{2-}$) was not excluded, a second experiment was performed with pure 0.1 M HNO$_3$ [60]. 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 and no SgO$_4^{2-}$ was formed. The non-tungsten-like behaviour of Sg in pure HNO$_3$ may be attributed to its weaker tendency to hydrolyse [60,64,65]. 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$_2$O)$_{2+}$; see [7,10,35] for a detailed discussion.

(ii) Gas-phase chemistry

Sg is expected to be very refractory in the elemental state [61] but to form volatile halides, oxide halides, oxide hydroxides and carbonyls [66,67]. The formation and volatility of SgO$_2$Cl$_2$ and SgO$_2$(OH)$_2$ were successfully studied in isothermal gas-adsorption chromatography experiments [42,61,62]. Adsorption enthalpies were determined which quantify the observed sequence in volatility of MoO$_2$Cl$_2 >$ WO$_2$Cl$_2 \approx$ SgO$_2$Cl$_2$. The formation of SgO$_2$Cl$_2$ is typical for a group-6 element and in agreement with relativistic theory calculations [7]; different, however, from the formation of UCl$_6$.

An exciting new development paves the way to metal-organic compounds of SHEs. The breakthrough comes from the use of physical pre-separators. They allow the collection and a chemical reaction of single atoms of a SHE in a recoil transfer chamber (RTC) without the destructive interference from primary particle beams. Exploratory experiments performed with 4$d$ and 5$d$ elements showed that carbonyls are accessible for a wide range of elements [67].

Ground-breaking experiments on the formation, stability, volatility and detection of Sg(CO)$_6$ were performed with the cryo-thermochromatography detector COMPACT [32] coupled to the GARIS recoil separator of RIKEN [68] where pre-separated $^{265}$Sg is available at a rate of about one-atom-per-hour for chemical investigations [63]. This experiment demonstrated atom-at-a-time the formation (even at a low CO pressure), separation and detection of Sg(CO)$_6$ [69]. Similar adsorption temperatures of Sg(CO)$_6$ and W(CO)$_6$ on Au surfaces were measured and adsorption enthalpies were deduced. These experiments open up new perspectives. Even though compounds with carbonyls are often not considered to be organometallic ones, these experiments show the route into the new field of organometallic chemistry of SHEs.

(c) Hassium (Hs, element 108)

Hassium, located in group 8 of the PTE, exploits the highest possible oxidation state (8$^+$) while forming the volatile HsO$_4$ [44,49]. Its volatility facilitated nuclear studies with unprecedented sensitivities giving access to $^{269}$Hs, the doubly magic $^{270}$Hs, the new isotope $^{261}$Hs and the confirmation of the discovery of Cn [19,70]. The 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 $\approx$3 atoms per day.

The successful Hs chemistry [44] set a milestone in SHE chemistry, making chemical studies of isotopes with half-lives of seconds produced with cross sections of a few picobarn possible. It was unique in a number of aspects: (i) a rotating wheel with $^{248}$Cm targets was applied for the first time in SHE chemistry to accept higher beam intensities [46]. (ii) A chemical reaction with O$_2$ was performed ‘in situ’ in the recoil chamber. (A similar technique has been used earlier for lighter SHEs in high-temperature TC [11]) This allowed a fast and efficient transport of chemically pre-separated HsO$_4$ to (iii) newly developed c-TC detectors known as COLD [44], CTS [71] and COMPACT [32].
In the first experiment, seven nuclear decays of Hs isotopes were observed [44]. It was concluded that a relatively stable, volatile HsO₄ is formed that has reached the detector. For HsO₄, an adsorption position at (−44 ± 6)°C was determined, which compares with the one of OsO₄ at (−82 ± 7)°C. Monte Carlo simulations of the movement of the tetroxide molecules in the gas phase and their wall-adsorption behaviour yielded a higher negative adsorption enthalpy of HsO₄ when compared with the one for OsO₄. A higher negative adsorption enthalpy is often referred to as ‘lower volatility’. Theoretically unexpected, this result triggered theoretical work. Now, good agreement is achieved [72]. These experiments were the first showing that SHE chemistry can be performed on a one-atom-per-day scale.

(d) Copernicium (Cn, element 112) and flerovium (Fl, element 114)

Element 112, Cn, located below Hg in group 12 of the PTE, is an especially fascinating element due to its 6d⁸⁷s² closed-shell configuration and a strong relativistic stabilization of the 7s orbitals. The question how closely Cn (in the atomic state) would resemble the behaviour of Hg attracted much attention [33,45]. Relativistic calculations indicated the possibility that Cn is rather inert, almost like a noble gas. In addition to its chemical reactivity, the possibility was discussed that, under ambient conditions, Cn can be a gas or a very volatile liquid (metal) [73]. Recent calculations [74–76] predict that a very volatile Cn would still retain a metallic character which would allow bond formation with metallic surfaces like Au [76]. On inert surfaces, however, no adsorption is expected [75]. From empirical correlations, an adsorption enthalpy range from −30 to −60 kJ mol⁻¹ was predicted for Cn on Au, to be compared with about −29 and −98 kJ mol⁻¹ for Rn and Hg, respectively [77,78].

First attempts to chemically study Cn are summarized in [49]. A breakthrough was obtained at the FLNR [28,29] when the reaction ⁴⁸Ca on ²⁴²Pu was used to produce 0.48-s ²⁸⁷Fl [24]. Its α-decay daughter 3.8-s ²⁸³Cn was transported in a He/Ar gas mixture within about 2 s to an improved COLD. In the first part of the experiment, COLD was operated at a temperature range from −24°C to −184°C and between +35°C and −180°C in the second one. Two α-decay chains assigned to ²⁸³Cn were observed: one in the first part at −28°C, directly in the deposition zone of simultaneously produced Hg, and one in the second part at −5°C. Because of a higher starting temperature and a shallower temperature gradient in the second experiment most of the Hg was deposited above −5°C. Simultaneously produced Rn was deposited far below −100°C on the cold end of COLD or passed through. This experiment provided the first and independent confirmation of nuclear decay chains reported earlier [24]. A third experiment [30], carried out with a higher gas-flow rate, observed two atoms of ²⁸³Cn deposited at −29°C and −39°C, respectively, and one at −124°C on the ice covered part of COLD. The analysis of these results gave an adsorption enthalpy of (−52 ± ₃) kJ mol⁻¹ (68% c.i.) for Cn on Au [30]. These experiments show that Cn is sufficiently volatile for a ‘gaseous’ transport (like Hg and Rn) to the detector. Contrary to Rn and more similar to Hg, Cn exhibits a metallic character shown by the formation of a Cn–Au metal–metal bond which, however, is weaker than the Hg–Au bond. Additional atoms of Cn were observed in the course of Fl chemistry studies at the FLNR [31] and at the GSI [32]; see below. All experimental findings on Cn [49] are in agreement with a fully relativistic 4c density functional theory calculation [76]. Extrapolated and theoretically calculated sublimation enthalpies can be found in [30,76].

The elements 113 and 114 mark 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 homologues [7]; a trend which also results from empirical correlations [50]. The volatility and reactivity of Fl was in the focus of many theoretical calculations [7,33–36,76] not only because Fl is often considered the showcase SHE, but also because the strong relativistic stabilization of the 7p¹/₂ orbital leads to a quasi-closed shell 7s²7p¹/₂ ground state. From this, a high volatility and chemical inertness was inferred culminating in Pitzer’s question ‘Are elements 112, 114 and 118 relatively inert gases?’ [73].
The discovery of 0.48-s $^{287}$Fl, produced with a cross section of 3.5 pb in $^{242}$Pu-based reactions and of 0.69-s $^{288}$Fl and 2.1-s $^{289}$Fl [24], accessible with cross sections up to about 10 pb [25,26] in $^{244}$Pu-based reactions, enabled chemical studies of Fl. Empirical extrapolations [50] and recent relativistic theory [75,76] predict that Fl is much more volatile than Pb but less volatile than Cn. It is also expected that Fl is chemically more inert than Pb but still has a pronounced metallic character, i.e. forms metal–metal bonds with Au. Thus, c-TC detectors developed and applied for studies of HgO$_4$ and Cn were implemented in Fl studies. Series of experiments were performed at the FLNR [31]. The observation of one decay in a Cn experiment, assigned to $^{287}$Fl and observed at the rather low temperature of $-88^\circ$C [31], came as a surprise because of the 0.48 s half-life of $^{287}$Fl and a mean transport time of 2.2 s. If characteristic for Fl, this adsorption position would indicate less metallic and more volatile properties than expected. Two additional events, assigned to $^{288}$Fl and observed at deposition temperatures of $-4^\circ$C and $-90^\circ$C, were seen in subsequent experiments with $^{244}$Pu as a target [31]. Because of a substantial background in the COLD, which was coupled to a recoil chamber directly behind the target, the significance of some of these events to decays of Fl was questioned [79]. But even if one accepts all nuclear decay assignments made in these experiments one ‘chemical’ problem remains. The deduced adsorption enthalpy of $-34$ kJ mol$^{-1}$ for Fl 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$^{-1}$ [76]. However, the error bands associated with the experimental findings ranging from $-31$ to $-54$ kJ mol$^{-1}$ and $-23$ to $-88$ kJ mol$^{-1}$ for a 68% and 95% c.i., respectively, brackets the observed behaviour of Fl between Hg and Rn [31]. Thus, no final conclusion on a metal-like character of Fl and its volatility in comparison with Cn can be drawn from these pioneering experiments.

The chemistry experiment performed at the GSI [32] with $^{288}$Fl and $^{289}$Fl circumvented two major problems. By using TASCA [80] as a pre-separator [79,81], Fl was isolated in-flight from unwanted nuclear decay background. 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 relevant while probing adsorption temperatures differences in less volatile elements. The direct coupling of COMPACT to the TASCA-RTC also allowed for a very short transport time of $(0.81 \pm 0.06)$ s. The adsorption behaviour of Fl, its $\alpha$-decay daughter Cn, their lighter homologues Pb and Hg and the noble gas Rn were studied simultaneously in a gas-chromatography experiment [32]. Two Fl atoms were detected; one decay was assigned to $^{288}$Fl and one to $^{289}$Fl. Both appeared at room temperature in detector #9 of the first COMPACT. These Fl events were separated from the main part of Pb and Hg observed at lower detector numbers. The volatility of Fl is demonstrated by the fact that it was transported in the flowing transport gas to the detector. The reactivity of Fl is evaluated from its adsorption on an Au surface at room temperature, where Cn does not adsorb as readily as Pb and Hg. This indicates that Fl is less reactive than Pb. A minimum value of the (negative) adsorption enthalpy of greater than 48 kJ mol$^{-1}$ was determined [32]. This reveals the metal–metal bond character for the Fl adsorption on Au surface. The Fl–Au metal–metal bond is at least as strong as the Cn–Au one. The rather volatile Fl is the least reactive element in group 14—but still a metal—and not as inert as a noble gas. This behaviour is in agreement with recent fully relativistic calculations on the adsorption of Fl on an Au surface [76,82] but disagrees with an interpretation of adsorption of Fl on Au surface merely due to physisorption [31].

5. Conclusion

Chemistry has reached the long dreamed of and highly desired SHE 114. As exciting as it is, however, only very first steps have been made to unravel the often surprising chemical properties of SHEs, to probe the influence of pronounced relativistic effects and electron-shell effects on atomic and chemical properties, to challenge most advanced fully relativistic theoretical model calculations and to map the architecture of the periodic table at its farthest reach. This atom-at-a-time chemistry of short-lived atoms and ions down to the scale of one atom per week is a great success and the result of enormous technological developments of sophisticated and
automated separation and detection devices. A wealth of new and fascinating chemical properties is waiting to be disclosed not only to satisfy the curiosity of chemists but even more to obtain a better understanding of the properties of matter at its limits—and where the limits are.

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