GSI-Preprint-95-49
SEPTEMBER 1995

CHEMISTRY OF THE TRANSACTINIDE ELEMENTS

M. SCHÄDEL

Gesellschaft für Schwerionenforschung mbH
Postfach 110552 · D-64220 Darmstadt · Germany

Chemistry of the Transactinide Elements

By Matthias Schädel

Gesellschaft für Schwerionenforschung, D-64291 Darmstadt, Germany

*Transactinides, Element 104, Element 105, Element 106, Periodic Table,
Atom-at-a-time chemistry, Heavy element synthesis, Molecular calculations*

Abstract

The experimentally known chemical properties of the transactinide elements 104 and 105, and the experimental techniques used to study these properties on an atom-at-a-time base, are reviewed. The production of transactinides in heavy ion reactions and the specific aspects of chemical separations with single atoms is briefly discussed. The chemical properties of the first two transactinide elements are compared with the lighter element homologs in group 4 and 5 of the Periodic Table and with the expected behaviour obtained from most recent atomic and molecular calculations which take the increasingly strong relativistic effect into account. Elements 104 and 105 behave as transactinide elements and, in general, exhibit properties characteristic of their position in group 4 and 5 of the Periodic Table. However, surprising deviations of the chemical properties from expectations based on simple extrapolations have been observed. It is shown that the chemical properties of the heaviest elements cannot reliably be predicted by simple extrapolations. Prospects to extend our chemical knowledge at the top end of the Periodic Table are discussed.

1. Introduction

It was Wilhelm Conrad Röntgens discovery of the X-rays in November 1895 which gave Henri Becquerel's research a new scope. He was motivated by his ambition to clarify the character of the X-rays and to find a link to his own scientific field, the study of phosphorescent bodies. Only a few months later, in 1896, Henri Becquerel discovered a new radiation [1]. Becquerel's discovery pushed the door wide open for a new science. Already two years later, in 1898, Pierre and Marie Sklodowska Curie interpreted Becquerel's observation correctly as an atomic phenomenon, coined the term "Radio-active" [2], and found the two new chemical elements polonium and radium.

In the centenary since Becquerel's discovery and half a century after Glenn T. Seaborg introduced the actinide concept [3] the Periodic Table of the Elements was completed and extended, see Fig. 1. Since the recent discovery of elements 110 and 111 [4,5] we know 19 man-made transuranium elements. The first 11 artificial elements beyond uranium belong to the actinides. Their chemistry is documented in a large number of books and articles, including the ones appearing in this volume. Additional overviews can be found in [6–8]. All experimental findings about the chemistry of element 103, lawrencium (Lr), show that, as expected, the actinide series ends at Lr and that a new 6d transition series begins with element 104, rutherfordium (Rf) ¹. Hence, the currently known eight transactinide elements have been placed in the Periodic Table under their lighter homologs of the 5d series Hf, Ta, Re, Os, Ir, Pt, and Au.

Investigating the chemical properties of the transactinide elements, both experimentally and theoretically, is the most important and challenging goal to determine the architecture of the Periodic Table at its upper end. Increasing deviations from the periodicity of chemical properties based on extrapolations from lighter homologs in the Periodic Table have been predicted for some time, see e.g. [9], as a consequence of increasingly strong relativistic effects. They originate from the increasingly strong Coulomb field of the highly-charged atomic nucleus. Thus, electron configurations different from those usually responsible for the chemical behaviour of the lighter homologs may become decisive in the transactinide elements. By a detailed comparison of their chemical behaviour with that of their lighter homologs, and by comparison with results of relativistic molecular-orbital (MO) calculations, it is hoped to explore the influence of "relativistic effects" in the chemistry of the heaviest elements.

The pioneering studies of some basic chemical properties of element 104 showed

¹Until unanimously accepted final names for the heaviest elements are recommended by the International Union of Pure and Applied Chemistry, the names endorsed by the Nomenclature Committee of the American Chemical Society for use in the U.S. are employed in this article without any prejudice about the priority in the discovery. It shall be noted that the names kurchatovium (Ku) and nielsbohrium (Ns) were used in some of the original publications of the Dubna group for elements 104 and 105. Since 1992 nielsbohrium (Ns) is used for element 107 leaving hahnium (Ha) for element 105.

that it behaves like a transactinide element. In general, element 104 exhibits chemical properties similar to those of zirconium and hafnium, as expected for an element located in group 4 of the Periodic Table, see Fig1. These early experiments exploited the chloride volatility in gas-phase experiments [10–13], and studied in aqueous solution the complexing behaviour of α -hydroxyisobutyrate (α -HIB) [14] and of chloride anions [15]. Although, all these were key experiments to demonstrate that the transactinides begin with element 104, none of these experiments enabled a detailed study of the rutherfordium chemistry. First generation gas-phase experiments with chlorides [16] and bromides [17,18] of element 105, hahnium (Ha), again indicated for the Ha halides a much greater volatility than that of the respective actinide compounds. These much higher volatilities of the Ha compounds are characteristic for a transactinide element. But these experiments also unveiled the lower volatility of the Ha compounds as compared with the ones from Nb, a lighter homolog in group 5. This gave the first hint that transactinide elements exhibit chemical properties which can not always be directly inferred from those of the lighter homologs. The first generation gas-phase separations with element 105, as earlier experiments on element 104, were plagued with model-dependent corrections of the observed deposition temperatures to deduce comparable volatilities. This was needed, because the deposition temperature depends strongly on the isotope half-life and on experimental parameters when using the thermochromatographic techniques [19,20]. Therefore, it was not possible to make detailed comparisons of the halide volatilities of the group 5 elements Nb, Ta, and Ha. The results from the first generation experiments on the transactinide elements were summarized in a number of review articles [21–24].

Since the late 1980s a renewed interest in studying in more detail the chemical properties of the transactinide elements has rejuvenated the entire field of research, both experimentally and theoretically, see [25–29] for recent reviews. The main thrust for series of new, and much more detailed experiments over the last decade mainly came from new technical developments of the experimental apparatuses. Computer-controlled automated systems have greatly enhanced the ability to perform rapidly and reproducibly large numbers of chromatographic separations on miniaturized columns in the liquid phase. A new quality of gas-phase experiments began with the development of transport and detection systems to identify unambiguously heavy-element nuclides through their characteristic α -decay *on-line* immediately after they have passed a gas-chromatographic column. This allows a much more direct comparison with the behaviour of the lighter element homologs. Simultaneously with the manifestation of interesting and sometimes surprising new experimental results also new developments of relativistic quantum-chemical codes at the Dirac-Fock level took place, and these are now becoming capable of modelling complex molecules.

In this article, a brief discussion of the synthesis and decay of the transactinide elements and a short section about specific aspects of the single-atom chemistry will precede an outline of recent developments of the experimental techniques. This will be followed by a review on the results of both aqueous and gas-phase studies of the heaviest elements investigated, elements 104 and 105. Current attempts and

prospects for studies of still heavier elements are briefly considered.

2. Synthesis and decay of transactinide elements

The synthesis of transactinide elements depends on nuclear fusion reactions with heavy ion beams. Details of the production and the decay of the heaviest-element nuclides are discussed in this volume [30], and were summarized in a number of review articles [31–37]. Product yields are rapidly decreasing from about one atom per minute for element 104 to about one atom per day for the heaviest man-made element with atomic number 111 [5]. Half-lives decreasing from about one minute to one millisecond for the longest-lived known isotopes of these elements pose an additional challenge, especially for chemical investigations. All transactinides have both short half-lives and such low production rates that, on the average, each synthesized atom has decayed before a new one is made. The term 'one-atom-at-a-time' was coined for this situation. Its consequences for chemical investigations will briefly be discussed in the next section.

The heaviest elements were synthesized with highest cross-sections in reactions with ^{54}Cr , ^{58}Fe , ^{62}Ni , and ^{64}Ni projectiles together with targets of ^{208}Pb and ^{209}Bi . Except for 4-s ^{257}Rf and 3-s ^{258}Ha , only nuclides with half-lives of less than one second are produced in these reactions. This is too short for existing chemical techniques of transactinide research. Their speed and efficiencies allow sensitive chemical studies with radionuclides of a few seconds half-life, and some techniques require a half life of at least ten seconds; see below for a detailed discussion. More neutron-rich and, hence, longer-lived nuclides are accessible in heavy-ion reactions with actinide targets. Typical experimental conditions are heavy-ion beam currents of 3×10^{12} particles per second and a maximum useful target thickness of about $700 \mu\text{g cm}^{-2}$. Recent chemical studies of element 104 use the longest-lived known isotope 65-s ^{261}Rf produced in the $^{248}\text{Cm}(^{18}\text{O}, 5n)$ reaction with a cross section of 5 nb. Abundant use of 34-s ^{262}Ha , and partially of 27-s ^{263}Ha [38,39], is made to shed light on the chemistry of element 105. These isotopes are synthesized in 5n- and 4n-reactions of ^{18}O beams on ^{249}Bk targets with a cross section of 6 nb and 2 nb, respectively. These cross sections yield production rates of the order of one atom per minute. Thus, all chemical procedures with transactinide elements are truly performed with single atoms, or "one-atom-at-a-time" [23,26].

Recent successes to synthesize the more neutron-rich isotopes ^{265}Sg and ^{266}Sg [40] of element 106, seaborgium (Sg), with deduced half-lives of the order of ten seconds, and cross sections of up to a few hundred picobarns, have paved the way to extend our knowledge about the chemistry of the heaviest man-made elements in future experiments. Nuclides with half lives sufficiently long to explore the chemistry of elements beyond $Z=106$ can, presumably, be found around the neutron number 162 for elements up to $Z=107$ and, possibly, in the $N \leq 174$ region for elements 108 through 114 [41]. Provided that nuclear reactions are at hand to produce these nuclides with cross sections of at least several tens or hundreds of picobarns, chemists can hope

to get insights into the chemistry of transactinide elements beyond seaborgium. See [37] for more details of the nuclear aspects of transactinide chemistry.

3. Single-atom chemistry

The one-atom-at-a-time situation of the transactinides poses some unique problems for the chemistry at the top end of the Periodic Table. The classical law of mass action is no longer valid [42,43] because a single atom cannot exist in different chemical forms taking part in the chemical equilibrium at the same time. For single atoms the concept of chemical equilibrium needs to be substituted by an equivalent expression in which concentrations or activities are replaced by probabilities to find the atom in one state or the other. The atom can sample these states with a high frequency of hundreds or millions of exchange reactions per second if the chemical system was selected such that the free enthalpy of activation is below 17 kcal [44]. The time one atom spends in one state or the other, 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 these two phases. This is realized in many chromatographic separations, e.g. in the exchange between a gaseous and a solid phase (wall adsorption) in gas chromatography or between a mobile aqueous phase and a stationary ion exchange resin in liquid chromatography. Here the retention or elution times provide the information about what fractional average time one atom has spent in either phase. Such a characterization of the behaviour of a single atom will already yield information close to the equilibrium constant which would be obtained from macroscopic amounts of this element.

4. Experimental techniques

A review on fast chemical separation procedures can be found in an accompanying article in this volume [45]. Here, only these techniques will be briefly outlined which are directly related to the chemical investigations of transactinide elements.

4.1. Production and transport

The target- and recoil-chamber arrangement is schematically shown in Fig. 2, and is described in more detail in [46,47]. Heavy-ion beams passed through a vacuum isolation window, a volume of nitrogen cooling-gas, and a target-backing before interacting with ^{248}Cm or ^{249}Bk as a target material. Reaction products recoiling out of the target were thermalized in a volume of helium loaded with 50 to 200 nm size aerosols to collect all products. As the first step common to all experiments, a continuous He flow ($\leq 2 \text{ l min}^{-1}$) through capillary tubes ($\approx 1.5 \text{ mm}$ inner diameter (i.d.)) provided a fast transport of the transactinides, and other reaction products, from the site of the heavy-ion reaction into the chemistry set-up. He(aerosol)-jets

allowed for a transportation over distances of up to several tens of meters with yields of about 50 % [47–50]. Overall transport times were of the order of two to five seconds.

So far, none of the experiments has exploited the potential of chemical reactions with the aerosols. Materials were selected to minimize their influence on the chemical procedures. Separations carried out in the aqueous phase used KCl as aerosols while MoO₃ or carbon was often preferred in gas-phase separations [51].

To circumvent problems with chemically interfering aerosol materials in some earlier frontal gas-chromatographic experiments the separation columns were directly coupled to the recoil chamber [52,53]. In such a configuration a still high enough transport yield can be achieved without using any aerosols. Transportation times as short as 0.1 second were measured [54], and the recoil chamber can simultaneously be used as a reaction chamber to form chemical compounds by adding a reactive gas to the inert carrier gas [55]. This technique, which was not used in recent gas-chromatographic studies, was applied in thermochromatographic separations to investigate the volatility of element 105 bromides [17] and in an attempt to determine the volatility of element 104 in its atomic state [56].

4.2. Gas-phase chemistry

Early gas-phase separations of elements 104 and 105 halides used the principle of thermochromatography, see [20] and references therein, in which a negative temperature gradient was formed along the chromatographic tube. Compounds with different volatilities separated from each other while moving downstream the column in the gas flow and deposited at a particular position inside the tube. These deposition zones at a given temperature are related to the adsorption enthalpy. The final region of deposition within the column was determined radiochemically for long-lived nuclides, e.g. for radioactive tracers of the lighter-element homologs. For short-lived isotopes of elements 104 and 105 fission-track detectors were used to determine the region of tracks from the spontaneous fission (SF) decay. Real-time detection of the nuclear decay of transactinides was not possible and the method was limited to fission-track counting which provided no unique signal about the nuclide or the element. Model dependent corrections were necessary to relate observed deposition temperatures of species with different half-lives to comparable volatilities.

More recent experiments used the isothermal gas-phase chromatography to study the retention times of Rf and Ha chlorides and bromides in real-time together with their lighter-element homologs [51,57]. The On-Line Gas Chemistry Apparatus (OLGA II) [49], and the Heavy Element Volatility Instrument (HEVI) [58], were the applied apparatuses, see Fig. 3 for a schematic layout of both systems. Reaction products continuously transported by the He(aerosol)-jet to a 6 mm i.d. quartz column were stopped in a quartz-wool plug located in the first, high-temperature section of the column. At temperatures of up to about 1000 °C the aerosol particles were destroyed and the heavy element formed a volatile compound with a reactive gas like HBr, BBr₃, HCl or Cl₂ added at this point with a flow rate of about 100-200

ml min⁻¹.

In earlier gas-phase separations, KCl was used as an aerosol material with the disadvantage that the KCl recondensed downstream in the colder, isothermal part of the column and the chromatography was, at least partially, carried out on a KCl surface [59]. In later experiments, MoO₃ or graphite aerosols were used [60]. This had the advantage that volatile species were formed which did not condense in the chromatographic column when chlorinating agents or oxygen were added as a reactive gas.

The second and much longer part of the quartz tube represented a lower and adjustable, isothermal temperature section for the gas-chromatographic separation. All compounds are transported through the column by means of the flowing He. The specific velocity of each compound depends on its volatility and on the temperature of the isothermal part of the column. The transit- or retention time of the volatile species was determined using the half lives of the radionuclides as a "clock". The measure for the volatility was the specific temperature $T_{50\%}$ at which the corresponding compound exited the chromatographic column with 50% yield. At this temperature, the retention time, as defined in classical gas chromatography, is equal to the half life. To measure the separated species, they were, at the outlet of the chromatographic column, ejected through an orifice into a recluster chamber. Here they reattached to new aerosols which were added for the transport of the separated products through a capillary to a detection set-up. Recent developments to miniaturize and cool the recluster chamber in OLGA III [61] have significantly reduced the time necessary for reattachment. Radionuclides with half lives between 1 and 4 s [62] became accessible with OLGA III.

The two different detection systems used in the gaschromatographic experiments were equipped with a rotating catcher wheel [63,58] or a tape system [49,64]. Both were operated stepwise to transport collected products in front of PIPS (passivated implanted planar silicon) detectors to measure characteristic α -decay energies and the kinetic energy of SF fragments. Thus, single atoms of ²⁶¹Rf and ²⁶²Ha were detectable. Only the rotating wheel was equipped with catcher foils thin enough to measure the nuclear decay on both sides of the foil. This gave the advantage of a high detection efficiency and allowed to measure the total kinetic energy of coincident fission fragments. The tape system had the advantage that, because of its length and the collection on unused spots, no long-lived background was building up which could have obscured the detection of single atoms of transactinide elements.

The energies of all observed events were stored together with a time and detector information for off-line processing of these data. This allowed to search for time-correlated parent-daughter pairs of α -events to assure an unambiguous identification of single events, see e.g. [38,64,39]

4.3. Aqueous-phase chemistry

While all separations in the gas-phase were carried out as a continuous process, so far mainly discontinuous, batch-wise chemical separations were performed in the aque-

ous phase. Recent discontinuous studies of the transactinides were either performed manually [48,65,66] or with the Automated Rapid Chemistry Apparatus (ARCA) [39,67-70].

While one of the manual separations made use of the characteristic adsorption of the group 5 elements Nb, Ta and Ha from nitric acid on glass surfaces [48] all other separations were manually performed liquid-liquid extractions. These procedures usually contained the following steps: reaction products were collected on a platinum or TeflonTM disc from the He(KCl)-jet for about 60 to 90 s, picked up with 10 μ l of the aqueous phase (mostly HCl or HNO₃ of various concentrations), transferred to a 1 ml centrifuge cone which contained 20 μ l of the organic phase, mixed ultrasonically for 5 s, and centrifuged for 10 s to separate the phases. The organic phase with one of the extractants methylisobutyl ketone (MIBK), triisooctylamine (TIOA), tributylphosphate (TBP), or 2-thenoyltrifluoroacetone (TTA) was transferred to a glass cover slip, dried on a hot plate, and placed over a PIPS detector. This procedure took about 1 min and was mainly applied to study the aqueous chemistry of element 104 with the 65-s ²⁶¹Rf [65,66].

Automated separations with ARCA II have focused on the investigation of the aqueous-phase chemistry of element 105 with the 34-s ²⁶²Ha. ARCA is a micro-computer controlled apparatus for fast, repetitive, and reproducible chromatographic separations in a miniaturized and chemically inert high-performance liquid-chromatography system [67]. A photograph of ARCA II is shown in Fig. 4. ARCA II consists of a central part to collect the aerosols from the jet and to perform chromatographic separations of the reaction products in 8 mm long micro-columns of 1.6 mm i.d.. Two movable magazines, in Fig. 4 partially protruding from the central part, contain 20 of these columns each. Depending on the chemistry, these columns were filled with a cation exchange resin (17.5 ± 2 μ m particle size Aminex A6) or with TIOA or diisobutylcarbinol (DIBC) as an organic extractant on an inert support material. Incorporated into the central part of ARCA II are three sliders. The one on top shuttles the reaction products after their collection alternating on top of one of the microcolumns, whereby the reaction products are dissolved, complexed, and loaded onto the column. Two sliders downstream of the columns allow to collect a Ha fraction on a Ta disc. The sample is dried by intense IR-light and a stream of hot He-gas. Peripheral components are three chemically inert chromatography pumps (not shown) and pneumatically driven 4-way slider valves (cylinders on top). Each pump pumps one pre-selected eluent through Teflon tubings to the 4-way valves. These allow a fast and reproducible stepwise changing of the eluents on the columns. The low dead volume of about 35 μ l including the free column volume gives a fast access to desired fractions. Within 3 s to 4 s, element 105 was separated from trivalent actinides and group 4 elements in a 35 μ l fraction of 0.05 M α -HIB, eluted from an Aminex A6 column [39]. In the most time consuming separation, Ha has been eluted after 25 s as the third eluent fraction from a TIOA column [68]. Sample preparation and mounting on PIPS detectors required about 20 s. Experiments with ARCA were performed in 1 min cycles. After each separation the magazine was moved by one step, thus introducing a new column in the

elution position. By this means, time-consuming reconditioning of used columns and cross-contaminations from previous separations are avoided.

First successful attempts were made to directly detect events from the α - and SF-decay from a thin film of solution in a large area PIPS-detector [39]. Start of counting was 0.8 s after end of collecting the reaction products on the top slider SL1, i.e. 0.8 s after the start of chemistry. This can be a useful technique as long as no high resolution α -spectroscopy is needed for a clear identification. To guarantee this, the chemical separation has to provide a clean fraction which does not contain any radionuclides showing similar or higher α -decay energies.

So far, only one continuous isolation procedure, first developed for nuclear decay studies of Hf, Ta, and W isotopes [71], was applied to an element 104 separation [72]. in combination with a discontinuous sample preparation step. Reaction products transported by an aerosol jet were continuously dissolved in an aqueous phase which was pumped through three consecutive ion exchange columns. Trivalent actinides were retained on the first cation exchange column followed by an anion exchange column to adsorb anionic complexes of element 104, and a third column filled with a cation exchange resin to collect all the trivalent daughter products from the α -decay of 65-s ^{261}Rf . At the end of an experiment, all element 104 daughter products were stripped from this third column to prepare a sample for the α -spectroscopy and to find out how strongly element 104 had been retained on the anion exchange column.

The centrifuge system SISAK III [73] allows a continuous separation of nuclides with half-lives down to ≈ 1 s. The separation is based on fast multistage solvent extractions using specially designed mini-centrifuges for phase separation. SISAK has successfully been applied to a large number of γ -spectroscopic studies of lighter elements. Most recently, a completely new detection system, based on liquid scintillation spectroscopy, was developed for on-line α -spectroscopy and SF-detection in a flowing liquid behind SISAK [74]. An energy resolution of 200 to 500 keV and a high β - and γ -suppression was achieved in preparatory experiments [75], and the entire set-up was put to a test in two experiments aimed to separate 2-s ^{262}Rf and 1.8-s ^{261}Ha [76]. Preparations are under way to apply this system for an on-line separation and detection of ^{266}Sg with SISAK [77].

5. The theoretical situation in general

At present each comparison of experimental results and theoretical calculations will always involve empirical systematics because no theoretical apparatus is at hand which can directly compute the chemical behaviour. The present situation of theoretical models and their application to the transactinide chemistry is reviewed in [78,79].

On the atomic level, early relativistic calculations for atoms and ions [80–83] have already shown that there is a strong relativistic stabilization of $s_{1/2}$ - and $p_{1/2}$ -orbitals as a function of atomic number, and, as a secondary effect, a destabilization of d-orbitals and their spatial expansion. On the current level of multiconfiguration

Dirac-Fock (MCDF) calculations important information about electronic configurations, ionization potentials, promotion energies, and atomic and ionic radii were obtained [84-88]. One of the important roles of atomic data from the MCDF calculations are their contribution as key input data to predict chemical properties, like oxidation states or volatilities, based upon empirical models which mainly exploit thermodynamic correlations, see e.g. [23]. However, it will not be possible to find any straightforward correlation between computable atomic properties and the chemical behaviour of a heavy element. This is, because the interplay of s-, p-, d-, and f-orbitals can change molecular properties like the relative amount of ionic versus covalent bonding, the bond length in the molecule, and the effective charge of the central atom. These for the chemistry decisive quantities are not directly extractable from the atomic calculation.

With progress in molecular calculations, especially from the Dirac-Slater (DS) calculations using the relativistic Discrete Variational Method with self-consistent charge (SCC) approximation [89,90] much more refined approaches begin to appear for a better theoretical understanding of the chemistry of the transactinide elements. For example, a lower effective charge on the central atom and a higher covalency in the bonding, as obtained in such calculations, strongly indicated that chlorides and bromides of transactinides are more volatile than their lighter homologs in group 4 and 5 of the halides [85,90,91]. However, theory predicts already for element 105 a preferential formation of oxyhalides over the formation of pure halides [92], a tendency known for elements of group 6 and onward. Such a trend can lead to the formation of different compounds with different volatilities for the respective transactinide element as compared with its lighter homologs when halides and oxygen are simultaneously present in gas-chromatographic experiments. Unfortunately, a complete model to calculate volatilities from basic atomic and molecular structure data has, up to now, not been developed.

Molecular DS DVM calculations indicated [93] that the first three transactinide elements will be tetra-, penta-, and hexavalent as their lighter homologs. The stability of the maximum oxidation state, however, was predicted to decrease from element 104 to 106 [93].

Empirical correlations which completely rely on the known physicochemical properties of elements and their compounds in the groups and periods of the Periodic Table, e.g. [18,20,94,95], allow classical extrapolations of chemical properties of the transactinide elements. These extrapolations provide information on what would be expected if no increasingly strong relativistic effect would be present in the transactinide elements because only the weaker relativistic effect already present in the lighter elements is inherent in this procedure. Such data are important to judge how strong relativistic effects contribute to the observed chemistry of transactinide elements.

6. Element 104

6.1. Theoretical Predictions

According to the normal continuation of the Periodic Table, element 104 is expected to be a member of group 4 below Ti, Zr, and Hf with an electronic ground-state configuration of $[\text{Rn}] 5f^{14}6d^2 7s^2$. This configuration was also indicated by early relativistic calculations [81,82] in a Dirac-Fock computation with a single configuration approximation [81].

After multiconfiguration Dirac-Fock (MCDF) calculations had indicated that because of relativistic stabilization of the $p_{1/2}$ -orbital, the electronic structure of element 103 is $[\text{Rn}] 5f^{14}7s^2 7p_{1/2}$ rather than $[\text{Rn}] 5f^{14} 6d 7s^2$ [96,97] it was extrapolated that element 104 should have a $7s^2 7p^2$ rather than a $6d^2 7s^2$ configuration [23]. This raised the question whether element 104 might be a "p-element" with properties similar to Pb that has a ground state configuration of $[\text{Xe}] 5f^{14} 5d^{10} 6s^2 p^2$. It is important to note two crucial differences between the Pb and Rf configuration: contrary to element 104, Pb has a closed 5d-shell and a great energy gap of more than 4 eV between its ground- and next-higher state.

A more recent multiconfiguration Dirac-Fock (MCDF) calculation, using 468 jj-configurations, gave a (80 %) $6d 7s^2 7p$ ground-state configuration [84] with a level only 0.5 ± 0.2 eV higher consisting of the $6d^2 7s^2$ configuration (95 %). This calculation obtained the $7s^2 7p^2$ state 2.9 eV above the ground state. The $6d 7s^2 7p$ ground-state configuration was confirmed in a similar MCDF calculation [86] with an energy gap of 0.24 eV between the ground-state and next higher state.

Most recent atomic calculations with the relativistic coupled cluster method based on the Dirac-Coulomb-Breit Hamiltonian (CCSD) which include dynamical correlations [88] reverted to the $6d^2 7s^2$ configuration as the ground state of element 104. Here, the $6d 7s^2 7p$ state is 0.274 eV above the ground state. Contrary to earlier calculations [86,85] it is now assumed [88] that a 6d electron is first ionized instead of the 7p electron.

From MCDF calculations ionization potentials (IP), atomic radii, and ionic radii were deduced [86,85]. It was found that radii, orbital energies, and ground levels of ionized states of element 104 are similar to Hf but different from Pb and its homologs [85]. From this it was concluded that there is no basis for expecting any distinct "p-character" in the chemical properties of element 104 and that its chemistry will resemble the Zr and Hf chemistry. The authors of [85] calculated that the first IP of element 104 (6 eV) is lower than for Zr and Hf and should result in a relatively greater stability of the lower oxidation state and/or a lower volatility of binary compounds for monovalent Rf [85]. From a relativistic SCF- $X\alpha$ scattering wave Dirac-Fock computation for the tetrachloride molecule of element 104 a lower effective charge of the central Rf atom and a higher covalency in the bonding was obtained [85]. This could explain a higher volatility of RfCl_4 in comparison with ZrCl_4 or HfCl_4 .

The DS DVM was applied to study the electronic structure of (i) the tetrachlo-

rides of Pb and group 4 elements [98] and (ii) the highest chlorides of group 4, 5, and 6 elements [93]. These calculations agree that the electronic structures of RfCl_4 and HfCl_4 are similar and that the bonding is typical of the transition d-element compounds. Both calculations [98,93] show the same trend in the ionicity within the group: a decrease in the values of the effective charges from Zr to Hf and a small increase from Hf to Rf. These for very heavy elements most advanced molecular calculations [98,93] show the RfCl_4 to be a rather covalent compound, with the covalency being greater in RfCl_4 than in HfCl_4 . This leads to a stronger metal-ligand bond in RfCl_4 compared with HfCl_4 . RfCl_4 should be thermally more stable than ZrCl_4 or HfCl_4 [93]. In these compounds it is expected that the tetravalent state of element 104 will be predominant.

6.2. Experimental results

The pioneering chemical experiments on element 104 in the gas phase [11,12] showed that element 104 forms volatile chlorides, and that the Rf chloride is much more volatile than the actinide chlorides and similar to ZrCl_4 and or HfCl_4 [13,53]. This experimental series gave the first indication that element 104 behaves like Hf, and that it is a group 4 element. The strongly enhanced retention after having introduced KCl into the gas-solid column at 300 °C was taken as an indication that the tetrachloride was formed as the most stable compound [53]. After applying half-life corrections to the experimentally observed distributions for RfCl_4 a volatility was obtained similar or even slightly higher than the one for HfCl_4 [53,13]. Small differences in volatility were not observable in these experiments because of a steep temperature gradient, see Fig. 5.

Modern gas chromatographic experiments are apt to determine the relative volatilities between various elements more precisely and unambiguously through time- and energy-correlated events from the α -decay of mother and daughter nuclei [51]. Figure 6 shows the relative (maximum yield=100 %) chemical yield of volatilized Rf versus temperature in the isothermal section of the gas-chromatographic column in comparison with the behaviour of Zr and Hf chlorides [51,99,57]. MoO_3 -aerosols were used in the transport jet. The chlorinating gases are listed in the figure together with the respective elements. The solid lines in Fig. 6 resulted from Monte Carlo simulations [99,57] based on the microscopic model of gas-solid chromatography [19]. The simulation accommodated the influence of the carrier gas flow, the temperature distribution in the column, and the different half-lives of the investigated nuclei. Calculated was the expected yield of a large number of sample molecules of one chemical species with a given adsorption enthalpy (ΔH_a) at each isothermal temperature. A specific curve of yield vs. temperature resulted for each value of ΔH_a chosen as an input parameter. The curve for the ΔH_a value which best fits the measured data was chosen by a least-squares method, and these ΔH_a values are given in the insert in Fig. 6. To obtain a consistent set of adsorption enthalpies from various experiments, data from the literature were reanalyzed using a calculated value for the adsorption entropy (ΔS_a) according to [100], and all these

data were compiled together with the most recent experimental results [51,99,57].

The results for the volatilities of group 4 chlorides showed two groups: one with a higher volatility and ΔH_a of about -70 kJ mol^{-1} and a second one with a lower volatility and ΔH_a of -90 kJ mol^{-1} or lower. The Zr and Rf chlorides shown in Fig. 6 exhibit a similar and rather high volatility. Such a behaviour was thought to be characteristic for the pure tetrahalides ZrCl_4 and RfCl_4 . The lower volatility for the Hf compound was suggested to indicate that the oxyhalide compound HfOCl_2 instead of the pure tetrachloride was studied in this experiment [51,99]. The formation of oxyhalides as a function of oxygen content in the gas will be discussed in more detail for the group 5 elements, see below.

The compilation of reanalyzed adsorption enthalpies [51,99] indicated that in at least one of the previous experiments [11] the formation of the pure tetrahalide of Zr and Hf together with the formation of the Rf oxyhalide was observed. The formation of a Zr oxyhalide in a different experiment can also be inferred [51,99].

A first and preliminary result from a gas-chromatographic study of group 4 bromides indicated a lower volatility of the Rf bromide as compared with the chloride. The experimental result hinted to a higher volatility of the Rf bromide by about 100°C as compared with the Hf compounds [60]. In this experiment it was observed that the yield of, presumably, the tetrabromide of element 104 remained stable at temperatures above 300°C and that it steeply decreased between 200°C and 100°C . In the same experiment, the yield of Hf bromides dropped to about 60 % in the temperature range from 600°C to 550°C , remained constant from 550°C to 400°C , and then dropped to a level of a few percent at 300°C . The presence of two regions of sharply decreasing yield was taken as evidence for the formation of two different Hf compounds with two different volatilities. The HfBr_4 is a candidate for the compound with the higher volatility and HfOBr_2 for the one with the lower volatility. Zirconium was not included in this investigation. The results of this experiment are not conclusive and can only be taken as evidence (i) because of large error bars on the rutherfordium data, and, more important, (ii) because of the use of a $\text{He}(\text{KCl})$ -jet in this experiment, which may have covered the quartz surface of the chromatographic column with KCl leading to much higher retention temperatures [53,59].

A comparison of the chloride and bromide volatilities of group 4 element compounds exhibited, in general, a higher volatility of the chlorides. The summary of all experimental data showed that, within the presently achieved experimental resolution, no trend in the adsorption enthalpies, and, hence, no differences in the volatilities of the group 4 halides of Zr, Hf, and Rf can be observed as long as the same compound is formed [51]. This indicates that the measured volatilities are in agreement with results from the relativistic DS DVM calculations [93] while empirical extrapolations in group 4 predict [95] a slightly less volatile RfCl_4 [57]. So far, the chemical composition of the investigated species has not been governed decisively enough by the experiments performed until now. Further experiments under absolutely oxygen-free conditions, including the material of the chromatographic column, are needed before any final conclusion on the influence of the relativistic

effect on the volatility of element 104 halides can be drawn. It is also premature to conclude which group 4 element has the highest and which one has the lowest tendency to form a pure tetrahalide or an oxyhalide.

One experiment was carried out in the gas phase to probe a p-element like behaviour of element 104 in its atomic state [56]. It was speculated that a much higher volatility of element 104 as compared with the group 4 elements Ti, Zr, and Hf would indicate such a character. In analogy to a similar experiment on element 103 [101,102] the retention of element 104 was measured along a quartz column at 1170 °C in a hydrogen containing Ar carrier-gas. All fission tracks from the 2.6-h ^{256}Fm , an unwanted by-product produced in the nuclear reaction, and from 4.5-s ^{259}Rf were observed in a typical d-element region. A lower limit for the sublimation enthalpy of $\Delta H_{\text{S}}^{\circ}(\text{Rf}) \geq 370 \text{ kJ mol}^{-1}$ was determined. This result is in agreement with predictions [85,84,98] that despite of a possible $6d\ 7s^2\ 7p$ ground-state configuration the chemical properties of Rf will be similar to Hf.

The first aqueous phase separations of element 104 were carried out in a column liquid chromatography [14]. Rf was eluted together with Zr and Hf from a cation exchange resin with α -HIB. It behaved entirely different from No and the trivalent actinides which were retained on the column. To exclude hydrolysis reactions at low acidities the chloride complexation of Rf was investigated in an automated solvent extraction chromatography with the quarternary amine Aliquat 336 as a stationary phase and 12 M HCl as a mobile phase [15]. Under these conditions, Zr, Hf, and Rf extracted into the organic phase while trivalent actinides were not adsorbed on the column. The Rf, together with the Hf tracer, was then eluted with 6 M HCl. Although only 6 α -decays from ^{261}Rf were detected this experiment demonstrated that the chloride complexation of Rf is similar to Hf and much stronger than that of the trivalent actinides [15].

In an experiment which combined a fast, continuous separation of element 104 on an anion exchange column with the off-line detection of longer-lived daughter products it was shown that element 104, like Hf, forms stable anionic complexes in 0.2 M HF solution [72]. This result established additional evidence, that element 104 is a transactinide element which belongs into group 4.

It was a series of manually performed separations which recently enlightened new and interesting properties of Rf in aqueous solution [25,65,66]. Extraction studies with TIOA showed that anionic complexes of tetravalent Rf are nearly 100 % extracted from 12 M HCl as is Zr but not Th [65]. Cationic species were investigated by extraction into thenoyltrifluoroacetone (TTA). A distribution coefficient for Rf between those of Th and Pu indicated that the hydrolysis of element 104 is less than that for Zr, Hf, and Pu [103].

The effect of chloride concentration and pH on the extraction of Rf into tributylphosphate (TBP) in benzene and into triisooctylamine (TIOA) in benzene was compared with that of group 4 homologs Zr and Hf, the pseudo-group 4 element Th, tetravalent Pu, Nb as a member of group 5, and trivalent actinides. In general, Rf was found to behave as a group 4 element and, unlike the trivalent actinides, extracts efficiently as a neutral complex into TBP from concentrated HCl. Between

8 M and 12 M HCl Rf extracts better into TBP than does Hf. Surprising results were obtained when the chloride concentration was varied at constant $[H^+]$. Fig. 7 shows the distribution of ^{261}Rf , ^{95}Zr , ^{169}Hf , ^{228}Th , and ^{238}Pu into a TBP phase from an aqueous phase being 8 M in $[H^+]$ as a function of the Cl^- concentration [66]. In Cl^- concentrations above 10 M at constant $[H^+]$ of 8 M, the extraction of tetravalent Rf decreases and behaves differently from Hf and Th, and most like Pu^{4+} . This indicates that the chloride complexation of Rf is stronger than that of Hf and Th and similar to that of tetravalent Pu. Consequently, Rf forms neutral salt complexes more readily than Zr and Hf, and in TBP inextractable anionic species at higher Cl^- concentrations. The compound RfCl_6^{2-} was suggested as a candidate [25]. Extraction studies at a constant concentration of 12 M Cl^- showed that the Rf extraction is sharply increasing with increasing $[H^+]$ between 8 M and 12 M [66]. Such a behaviour is not exhibited by Zr and Hf.

As it was found earlier for element 105, see next section for details, also these results on the aqueous chemistry of element 104 indicate unexpected trends in the chemical behaviour of the transactinide elements as compared with classical extrapolations. This demonstrates that specific properties of the lighter homologs can not be simply extrapolated to obtain the chemical properties of the transactinide elements in detail. As some of the Rf extraction experiments suffered from small but possibly not unimportant differences in the chemical procedures applied to the individual elements, e.g. different contact times and volumes used, it is important to confirm these very interesting findings in an experiment that establishes identical separation conditions for all of these elements under investigation.

7. Element 105

7.1. Theoretical Predictions

A normal continuation in the Periodic Table puts element 105, hahnium (Ha), in group 5 below Ta. From this analogy to Ta, the electronic ground state configuration of Ha is expected to be $[\text{Rn}] 5f^{14}6d^3 7s^2$. This is in agreement with earlier relativistic calculations [82] and with the most recent MCDF calculation [87]. Contrary to elements 103 and 104, a dominating contribution of the $7p_{1/2}$ state is not expected for Ha. Atomic and ionic radii and the first through fifth ionization potentials were obtained in the MCDF calculations [87]. Differences in the chemical behaviour of element 105 as compared with the classically expected properties of eka-tantalum may possibly arise from (i) a greater atomic or ionic radius, (ii) differences in the covalency and the effective charges of the central ion, and/or (iii) differences in the radial extension of d-wave functions which are most important in molecular bondings [90–93,104,105].

Standard redox potentials were estimated for group 5 elements and the pseudo-group 5 element Pa on the basis of ionization potentials from MCDF calculations [87,106]. It was shown [106] that the stability of the pentavalent state is increasing

along the group from V to Ha, while that of the tetra- and trivalent state decreases in this direction. Although the stability of the maximum oxidation state is decreasing along the period from element 103 to 105, no extra stability of the trivalent state of Ha was found in the estimates [106]. It would be interesting to probe this prediction by reduction experiments. These could be carried out in aqueous solution similar to the experiments performed on element 103 [107].

Relativistic molecular DS DVM calculations allow to determine the degree of covalency in the bonding and the effective charge on the central metal atom in halide and oxyhalide compounds of the group 5 elements V, Nb, Ta, and Ha [90–92,104]. From the results of these calculations it was inferred [91] that HaBr_5 should have a higher volatility compared with its lighter homologs. Such a distinct higher volatility of HaBr_5 was not obtained in an extrapolation of physicochemical properties of elements and their compounds within the groups and periods of the Periodic Table [94]. Only the smaller relativistic effects which are already present in the lighter homologs are extrapolated in this approach which does not account for the increasingly strong relativistic effect in the heaviest elements. Generally, volatilities predicted from relativistic calculations are higher than those extrapolated from physicochemical properties [57].

The electronic structure of the group 5 element anionic complexes $[\text{MCl}_6]^-$, $[\text{MOCl}_4]^-$, $[\text{M}(\text{OH})_2\text{Cl}_4]^-$, and $[\text{MOCl}_5]^{2-}$, were calculated with the relativistic DS DV method [108]. The charge density distribution analysis showed (i) that Ta has the highest tendency to form the pure halide complex $[\text{TaCl}_6]^-$, (ii) that Pa has a strong $\text{Pa}=\text{O}$ bond in its oxyhalide complex, and (iii) that Nb and Ha show about equal trends to form the pure hexahalide and the oxyhalide complex. The preferential formation of $[\text{HaOCl}_5]^{2-}$ was expected at medium HCl concentrations. At the highest HCl concentrations $[\text{HaCl}_7]^{2-}$, like $[\text{PaCl}_7]^{2-}$, was expected to be the most stable species [108].

7.2. Experimental results

The volatilities of element 105 chlorides and bromides were first studied [16,17] with 1.8-s ^{261}Ha in a similar thermochromatographic set-up as was used for element 104. The results from these early studies of the bromides are shown in Fig. 8. In these experiments, the SF-track distribution along the column was assumed to characterize the element 105 behaviour. The measured distribution of ^{261}Ha was corrected for the much shorter half-life before comparing it with the adsorption zones of longer-lived tracer activities of various elements including 3.3-min ^{169}Hf to represent a group 4 behaviour and 14.6-h ^{90}Nb as a group 5 element.

It was apparent from these experiments (i) that element 105 behaves like a typical transactinide element, (ii) that the chlorides and bromides of element 105 are less volatile than the Nb compounds, and (iii) that the element 105 compounds show a volatility which is rather similar to, or only slightly higher than the volatility observed for the Hf compounds (see above for a discussion of the Hf behaviour in group 4). The authors of the experiment concluded that element 105 is a homolog of the

group 5 elements Nb and Ta [16,17]. Their results were differently interpreted as showing that Ha behaves more like a group 4 element or, as an alternative interpretation, that these results much closer resemble the behaviour of the tetrachloride of V or the oxychlorides of V and Nb [21,109].

First gas-chromatographic studies on the bromides of the group 5 elements Nb, Ta, and Ha [51,59] were performed with the OLGA II set-up [49]. The results are shown in Fig. 9 where the chemical yield at a given temperature is a measure for the volatility. The curve for Nb was measured with pure HBr as a brominating agent, for Ta with HBr containing BBr₃ vapor, and for Ha with both, pure HBr and HBr with BBr₃ vapor. These data seem to establish that the bromides of Nb and Ta have a similar volatility while the Ha bromide is less volatile. Good agreement was found with reanalyzed earlier thermochromatographic data [99]. However, both sets of experimental results seem, at the first glance, to disagree with results from relativistic molecular calculations [91]. Theory predicted that HaBr₅ has the highest covalency and lowest effective charge among the group 5 bromides which should make HaBr₅ more volatile than its homologs. Also a "non-relativistic" thermodynamical model [94] estimated a band of possible HaBr₅ volatilities which are close to the NbBr₅ and TaBr₅ volatilities. This situation is depicted in Fig. 10. Here, the vapor pressures as a function of temperature [51,91] are used as a measure of the relative bromide volatility.

The current interpretation of the observed low Ha-bromide volatility assumes the formation of an oxybromide compound like HaOBr₃. This is supported by theoretical calculations which showed for Ha a much stronger tendency to form oxyhalide compounds as for Nb and Ta [92]. While the generally lower volatility of the oxyhalide compounds can be inferred from the DS DVM calculations it remains open whether the HaOBr₃ volatility will be higher or lower than that of Nb and Ta oxyhalides [92]. Further experiments are needed for a comparison of all group 5 oxybromides. This would enable theory to determine which interaction is determining the volatility of Ha halides [92].

In a first series of experiments to investigate the chloride compounds of group 5 elements in the gas phase, it was observed that Ha chlorides are more volatile than their respective bromides, probably similar in volatility to NbCl₅ [110,57]. This is in agreement with the finding that the group 4 and 5 chlorides are more volatile than the respective bromides. For Ta, only a species with a much lower volatility was observed, presumably TaOCl₃ [57].

In a most recent experiment [57] precautions were taken to reduce the partial pressure of free O₂ as far as possible. Carbon aerosols were used in the He-jet to transport the reaction products into OLGA III. Purified HCl was added as a chlorinating agent. The relative yield curves for Ha chlorides are shown in Fig. 11 together with yield curves measured for NbCl₅ and NbOCl₃ under identical conditions [57]. The Monte Carlo simulations (solid line in Fig. 11) reproduced the positions and shapes of the measured yields very well. The yield curve for Ha chlorides was analyzed assuming that two chemical species were present, namely HaCl₅ and HaOCl₃ [57]. Compared with NbOCl₃, HaOCl₃ became volatile at an approximately 50 °C

higher temperature. This is in qualitative agreement with extrapolations within the Periodic Table. An investigation of the Ta-chloride volatilities is needed to complete the picture in group 5. Presently, only a lower limit can be given for the adsorption enthalpy of HaCl_5 . Future experiments are needed to extend the yield measurements of Ha chlorides to lower temperatures for a comparison with theoretical predictions. Both methods, the DS DVM calculation and the empirical extrapolation predict the HaCl_5 as being equally or even more volatile than NbCl_5 .

The first aqueous chemistry of element 105 was an experiment to study the adsorption onto glass surfaces after fuming twice with concentrated HCl and HNO_3 solutions [48]. In manual separations, it was shown that Ha adheres with high yield to glass surfaces from HNO_3 solution, a behaviour very characteristic for the group 5 elements Nb and Ta and for Pa as a pseudo-group 5 element. The next experiment was an attempt to study the extraction of Ha fluoride complexes from a mixture of HNO_3 and HF into MIBK [48] under conditions in which Ta extracts but Nb does not. From an extrapolation in group 5 it was expected that Ha would behave more like Ta than Nb but, surprisingly, Ha did not extract.

To investigate this unexpected finding and more facets of the Ha chemistry in greater detail, on-line separations were conducted with the Automated Rapid Chemistry Apparatus ARCA II [67]. In the first experiments, liquid extraction chromatography separations were performed with the anion exchange liquid TIOA on an inert support [68]. Preparatory tests had shown that TIOA extracts all group 5 elements and Pa, irrespective of the formation of mono- or polynegative anions, from HCl solutions of 10 M and above. At lower concentrations, the selective back extraction allowed to distinguish between the chemical behaviour of Nb, Ta, Pa, and Ha. A diagram of the results from the chromatographic separations of Ha and its lighter homologs is given in Fig. 12. Element 105 was shown [68] to extract into the TIOA on the chromatographic columns in ARCA from (i) either 12 M HCl/0.02 M HF or (ii) 10 M HCl, as do Nb, Ta, and Pa. This result clearly indicated the formation of anionic Ha complexes. To obtain an element 105 fraction in this experiment, the amine, along with the extracted species, was stripped from the column with acetone/0.02 M HF, see upper panel in Fig. 12, and from this fraction a sample was prepared for the α -spectroscopic identification of ^{262}Ha . Elution positions of element 105 relative to those of Nb, Ta, and Pa were determined [68] in 10 M HCl/0.025 M HF (lower panel in Fig. 12), in 4 M HCl/0.02 M HF (middle panel), and in 0.5 M HCl/0.01 M HF [70] (not shown). In some experiments, 6 M HNO_3 /0.015 M HF was used to complete the back extraction of Ha into the mobile aqueous phase.

At HCl concentrations of 4 M and above, Ha was found to behave similarly to Nb and Pa while at the lower concentration of 0.5 M HCl Ha follows the pseudo-group 5 element Pa in its behaviour. The results of these chromatographic studies of Ha are plotted (bars) in Fig. 13 as the percentage extraction together with results from batch extractions performed with tracers of the lighter homologs (curves).

At all HCl concentrations below 12 M, Ha was found to behave differently from its closest homolog Ta. Apparently, in contrast to straightforward extrapolations, the trend in the chemical properties of the group 5 elements from Nb to Ta does

not continue but is reversed in going from Ta to Ha. This is mainly because of the exceptional behaviour of Ta within group 5. Only for Ta, strong largely covalent complexes of the pure halide type such as $[\text{TaX}_6]^-$ ($\text{X} \equiv \text{Cl}, \text{F}$) are predominant over a wide range of HCl concentrations. From the non-Ta-like behaviour of element 105 and its similarity to Nb and Pa, it was concluded [68,70] that the complex structure of Ha must be of the Nb and Pa type, presumably $[\text{HaOX}_4]^-$, in hydrolysis equilibrium with $[\text{Ha}(\text{OH})_2\text{X}_4]^-$, or $[\text{HaOX}_5]^{2-}$. This preferential formation of oxyhalide complexes of element 105 is in agreement with results from relativistic DS DVM calculations [108]. The oxygen-containing complexes have higher effective charges and carry dipole moments, both contributing to a lower extractability of these ions into the TIOA as compared with the largely covalent and therefore more hydrophobic $[\text{TaX}_6]^-$ [108,28]. The formation of $[\text{HaX}_7]^{2-}$ in concentrated HCl, as expected from theory [108], was not excluded in these experiments. The use of mixed HCl/HF solutions in these experiments prohibits a clear assignment to one specific complex, and it clearly calls for experiments with only one possible halide ligand. The non-Ta-like behaviour of Ha observed in the extraction experiments with MIBK [48] can be understood in the frame of these results as the procedure was specific for Ta and did not include a Nb-like behaviour.

Extractions of Nb, Pa, and Ha into DIBC from concentrated HBr solutions showed [69] that the tendency to form polynegative anions is increasing in the sequence $\text{Pa} < \text{Nb} < \text{Ha}$. Elutions from cation exchange columns with unbuffered 0.05 M α -HIB solution showed that Ha, together with Nb and Ta, elutes promptly [39] while tri- and tetravalent ions are strongly retained under these conditions. This provided an unambiguous proof that pentavalent Ha is the most stable valence state in aqueous solution [39], and it supported the position of element 105 as a member of group 5 of the Periodic Table.

The chemistry of element 105, to a greater extent than the chemistry of element 104, provided many surprises. Its non-Ta-like behaviour and its similarity to Nb and/or Pa, depending on its chemical environment, demonstrated that the chemical properties of this second transactinide element cannot be reliably extrapolated from the trends observed in its lighter homologs.

8. The future - element 106 and beyond

Elements 106 through 112 are expected to complete the 6d transition series. As such they should be placed in groups 6 through 12 of the Periodic Table as homologs of the elements W through Hg. However, based on our experience with the transactinide elements 104 and 105, it appears that the electronic configuration of these elements will be difficult to predict from a simple extrapolation. From the relativistic stabilization of the s-orbitals it is expected that all transactinides will have a $7s^2$ -configuration. This was confirmed in a most recent atomic calculation [111] for element 111 which, in contrast to its lighter homologs in group 11, has a $6d^9 7s^2$ ground state configuration. However, the knowledge of the electronic

ground state configuration provides not enough information to predict the chemical properties of the heavier transactinides. In addition, these elements may possibly exhibit chemical properties which are in their details significantly different from simple extrapolations within their groups. It was pointed out [7,25] that the electronic orbitals in these elements are close enough in energy and extension that a great variety of chemical behaviours may result, in its diversity similar to the beginning of the actinide series. Some of the surprising facets of elements 104 and 105 chemistry may have given us the first glimpse of such diverse properties. Presently, it would be premature to expect that the general ordering principle of the Periodic Table will not hold anymore but more and more unexpected properties may be observable for elements 106 and beyond. A comparison with up-to-date atomic and molecular calculations, may reveal the contribution of the increasingly important influence of relativistic effects on the chemistry of the heaviest elements.

Existing separation technologies, like ARCA II [67], OLGA III [61,62], and SISAK III [73] with its newly developed on-line detection system [74], provide means to extend our studies of the transactinides to element 106, seaborgium (Sg). The discovery of the longer-lived isotopes ^{265}Sg and ^{266}Sg [40] has eased the situation of operating the separation apparatuses at their limits. Several attempts are under way to begin these investigations [77] with all three of the above mentioned techniques. The research goals are to determine the hexavalency of Sg ions and to characterize the formation and behaviour of oxyhalides in aqueous solution and in the gas phase. Results from DS DVM calculations are at hand [93,108,112] to compare experimental findings with theoretical predictions. This is planned to be complemented by a Sg extraction from α -HIB solution into trioctylamine. Reports about first results from a thermochromatographic separation of 0.9-s ^{263}Sg [113] were not unanimously accepted because of an equivocal assignment of the observed fission tracks.

Although elements 107 – 111 have been discovered by physical methods, none of these elements has been identified after chemical separation because of the very short half-lives of the presently known nuclides. A number of experiments have been prepared and tested to separate longer-lived isotopes of element 107, nielsbohrium (Ns), see [114,115] and references therein, and heavier elements. From our knowledge of heavy element nuclei it appears that longer lived species of the heaviest elements probably exist. The biggest problem now is to find the best method to synthesize these nuclei. One of the promising paths are heavy ion reactions with ^{254}Es as a target [37]. It will be intellectually most interesting and experimentally most challenging to extend chemical studies to still heavier elements to get further insights into the importance of relativistic effects on chemical properties at the top end of the Periodic Table. Ultimately, perhaps nuclear and chemical research may even reach the elusive island of spherical superheavy element around $Z=114$ and $N=178$.

Acknowledgments

It's a great pleasure to thank, among many other colleagues quoted in this article, H.W. Gäggeler, J.V. Kratz, and A. Türlér for many discussions and for providing me with several figures including the latest unpublished results. Enlightening discussions with V. Pershina about the theory of transactinide chemistry are gratefully acknowledged. I like to thank B. Schausten for preparation of many drawings and W. Bröchle for reading the manuscript.

References

- [1] Becquerel, H.: Compt. Rend. **122**, 420, 501, 559, 689, 762, 1086 (1896), and Compt. Rend. **123**, 855 (1896).
- [2] Curie, P., Sklodowska Curie, M.: Compt. Rend. **127**, 175 (1898).
- [3] Seaborg, G.T.: Chem. Eng. News **23**, 2190 (1945).
- [4] Hofmann, S., Ninov, V., Heßberger, F.P., Armbruster, P., Folger, H., Münzenberg, G., Schött, H.J., Popeko, A.G., Yeremin, A.V., Andreyev, A.N., Saro, S., Janik, R., Leino: Z. Phys. A **350**, 277 (1995).
- [5] Hofmann, S., Ninov, V., Heßberger, F.P., Armbruster, P., Folger, H., Münzenberg, G., Schött, H.J., Popeko, A.G., Yeremin, A.V., Andreyev, A.N., Saro, S., Janik, R., Leino: Z. Phys. A **350**, 281 (1995).
- [6] Seaborg, G.T.: Radiochim. Acta **61**, 115 (1993).
- [7] Katz, J.J., Seaborg, G.T., Morss, L.R.: *The Chemistry of the Actinide Elements*, 2nd ed., Chapman and Hall, London, 1986.
- [8] Seaborg, G.T., Loveland, W.D.: *The Elements Beyond Uranium*, John Wiley and Sons, Inc., New York, 1990.
- [9] Fricke, B., Greiner, W.: Phys. Lett. **30B**, 347 (1969).
- [10] Zvara, I., Chuburkov, Yu.T., Caletka, R., Zvarova, T.S., Shalaevsky, M.R., Shilov, B.V.: At. Energ. **21**, 8 (1966); J. Nucl. Energy **21**, 60 (1966); Sov. J. At. Energy **21**, 709 (1966).
- [11] Zvara, I., Chuburkov, Yu.Ts., Caletka, R., Shalaevsky, M.R.: Sov. Radiochem., **11**, 161 (1969).
- [12] Chuburkov, Yu.T., Zvara, I., Shilov, B.V.: Sov. Radiochem., **11**, 171 (1969).
- [13] Zvara, I., Belov, V.Z., Chelnokov, L.P., Domanov, V.P., Hussonnois, M., Korotkin, Yu.S., Shegolev, V.A., Shalaevsky, M.R.: Inorg. Nucl. Chem. Lett., **7**, 1109 (1971).
- [14] Silva, R.J., Harris, J., Nurmia, M., Eskola, K., Ghiorso, A.: Inorg. Nucl. Chem. Lett., **6**, 871 (1970).
- [15] Hulet, E.K., Loughheed, R.W., Wild, J.F., Landrum, J.H., Nitschke, J.M., Ghiorso, A.: J. Inorg. Nucl. Chem., **42**, 79 (1980).
- [16] Zvara, I., Eichler, B., Belov, V.Z., Zvarova, T.S., Korotkin, Yu.S., Shalaevskii, M.R., Shegolev, V.A., Hussonnois, M.: Sov. Radiochem. **16**, 709 (1974).

- [17] Zvara, I., Belov, V.Z., Domanov, V.P., Shalaevskii, M.R.: Sov. Radiochem. **18**, 328 (1976).
- [18] Zvara, I., 1976, In: *Transplutonium Elements*, eds. W. Müller and R. Lindner, North-Holland, Amsterdam, pp. 11-20.
- [19] . Zvara, I.: Radiochim. Acta **38**, 95 (1985).
- [20] Zvara, I.: Isotopenpraxis **26**, 251 (1990).
- [21] Keller, O.L. Jr., Seaborg, G.T.: Ann. Rev. Nucl. Sci. **27**, 139 (1977).
- [22] Hulet, E.K., 1981, In: *Actinides in Perspectives*, ed. N.M. Edelstein, Pergamon Press, Oxford, pp. 453-490.
- [23] Keller, O.L., Jr.: Radiochim. Acta **37**, 169 (1984).
- [24] Silva, R.J., 1986, In: *The Chemistry of the Actinide Elements*, eds. Katz, J.J., Seaborg, G.T., Morss, L.R., 2nd ed., Vol. 2, Chapman and Hall, London, pp. 1085-1117.
- [25] Hoffman, D.C.: Proc. *Fifty Years with Transuranium Elements*, The Robert A. Welch Foundation Conf. on Chemical Research XXXIV, Houston, TX, 22-23 October 1990, pp.255-274, and Lawrence Berkeley Laboratory Report **LBL-29815**, (1990).
- [26] Hoffman, D.C.: Radiochim. Acta **61**, 123 (1993).
- [27] Schädel, M., 1993, In: *Nuclei Far From Stability/Atomic Masses and Fundamental Constants 1992*, ed. R. Neugart and A. Wöhr, Institut of Physics Conf. Series 132, Institut of Physics Publ., Bristol, pp. 413-422.
- [28] Kratz, J.V.: Proc. Int. Conf. *Actinides-93*, Santa Fe, NM, 19-24 September 1993, Elsevier, Amsterdam (1994), and J. Alloy Comp. **213/214**, 20 (1994).
- [29] Hoffman, D.C.: Chem. Eng. News **72**(18), 24 (1994).
- [30] Münzenberg, G.: Radiochim. Acta, this volume
- [31] Armbruster, P.: Ann. Rev. Nucl. Part. Sci. **35**, 135 (1985)
- [32] Münzenberg, G.: Rep. Prog. Phys. **51**, 57 (1988)
- [33] Herrmann, G.: Angew. Chem. Int. Ed. Engl. **27**, 1417 (1988)
- [34] Reisdorf, W., Schädel, M.: Z. Phys. A - Hadrons and Nuclei **343**, 47 (1992)
- [35] Oganessian, Yu.Ts.: J. Alloy Comp. **213/214**, 50 (1994)

- [36] Münzenberg, G.: *The Prospects of Heavy Element Research* In: Frontier Topics in Nuclear Physics (W. Scheid, A. Sandulescu Edts.) Plenum Publ. Comp., New York, 1995 (in press)
- [37] Schädel, M., Hofmann, S.: J. Radioanal. Nucl. Chem., in press (1995)
- [38] Kratz, J.V., Guber, M.K., Zimmermann, H.P., Schädel, M., Bruchle, W., Schimpf, E., Gregorich, K.E., Türler, A., Hannink, N.J., Czerwinski, K.R., Kadkhodayan, B., Lee, D.M., Nurmia, M.J., Hoffman, D.C., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U.W., Weber, A.: Phys. Rev. C **45**, 1064 (1992).
- [39] Schädel, M., Bruchle, W., Schimpf, E., Zimmermann, H.P., Guber, M.K., Kratz, J.V., Trautmann, N., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U.W., Weber, A., Gregorich, K.E., Türler, A., Czerwinski, K.R., Hannink, N.J., Kadkhodayan, B., Lee, D.M., Nurmia, M.J., and Hoffman, D.C.: Radiochim. Acta **57**, 85 (1992).
- [40] Loughheed, R.W., Moody, K.J., Wild, J.F., McQuaid, J.H., Lazarev, Yu.A., Lobanov, Yu.V., Oganessian, Yu.Ts., Utyonkov, V.K., Abdullin, F.Sh., Buklanov, G.V., Gikal, B.N., Iliev, S., Mezentssev, A.N., Polyakov, A.N., Sedykh, I.M., Shirikovskiy, I.V., Subbotin, V.G., Sukov, A.M., Tsyganov, Yu.S., Zhuchko, V.E.: Proc. Int. Conf. *Actinides-93*, Santa Fe, NM, 19-24 September 1993, Elsevier, Amsterdam (1994), J. Alloy Comp. **213/214**, 61 (1994), and Lazarev, Yu.A., Lobanov, Yu.V., Oganessian, Yu.Ts., Utyonkov, V.K., Abdullin, F.Sh., Buklanov, G.V., Gikal, B.N., Iliev, S., Mezentssev, A.N., Polyakov, A.N., Sedykh, I.M., Shirikovskiy, I.V., Subbotin, V.G., Sukov, A.M., Tsyganov, Yu.S., Zhuchko, V.E., Loughheed, R.W., Moody, K.J., Wild, J.F., McQuaid, J.H.: Phys. Rev. Letters **73**, 624 (1994).
- [41] Smolanczuk, R., Skalski, J., Sobiczewski, A.: Preprint GSI-94-77 (1994)
- [42] Guillaumont, R., Adloff, J.P., Peneloux, A.: Radiochim. Acta **46**, 169 (1989).
- [43] Guillaumont, R., Adloff, J.P., Peneloux, A., Delamoye, P.: Radiochim. Acta **54**, 1 (1991).
- [44] Borg, R.J., Dienes, G.J.: J. Inorg. Nucl. Chem. **43**, 1129 (1981).
- [45] Trautmann, N.: Radiochim. Acta, this volume
- [46] Nitschke, J.M.: Nucl. Instrum. Methods **138**, 393 (1976).
- [47] Schädel, M., Bruchle, W., Haefner, B.: Nucl. Instrum. Methods in Phys. Res. **A264**, 308 (1988).
- [48] Gregorich, K.E., Henderson, R.A., Lee, D.M., Nurmia, M.J., Chasteler, R.M., Hall, H.L., Bennett, D.A., Gannett, C.M., Chadwick, R.B., Leyba, J.D., Hoffman, D.C., Herrmann, G.: Radiochim. Acta **43**, 223 (1988).

- [49] Gäggeler, H.W., Jost, D.T., Baltensperger, U., Weber, A., Kovacs, A., Vermeulen, D., Türlér, A.: Nucl. Instrum. Methods in Phys. Res. **A309**, 201 (1991).
- [50] Günther, R., Becker, H.U., Zauner, S., Nähler, A., Kratz, J.V., Schädel, M., Bröchle, W., Jäger, E., Schimpf, E., Schausten, B.: Institut für Kernchemie, Univ. Mainz, Jahresbericht 1994, IKMz 95-1 (1995) p. 7.
- [51] Gäggeler, H.W.: J. Radioanal. Nucl. Chem. **183**, 261 (1994)
- [52] Chuburkov, Yu.T., Belov, V.Z., Caletka, M., Shalaevsky, M.R., Zvara, I.: Sov. Radiochem. **11**, 386 (1969), and Chuburkov, Yu.T., Zvara, I., Shilov, B.V.: Sov. Radiochem. **11**, 171 (1969).
- [53] Zvara, I., Chuburkov, Yu.T., Belov, V.Z., Buklanov, G.V., Zakhvataev, B.B., Zvarova, T.S., Maslov, O.D., Caletka, R., Shalaevsky, M.R.: J. Inorg. Nucl. Chem. **32**, 1885 (1970).
- [54] Belov, V.Z., Zvarova, T.S., Shalaevsky, M.R.: Sov. Radiochem. **17**, 87 (1975).
- [55] Zvara, I., Keller, O.L.Jr., Silva, R.J., Tarrant, J.R.: J. Chromatogr. **103**, 77 (1975).
- [56] Zhuikov, B.L., Chuburkov, Yu.T., Timokhin, S.N., Kim U Jin, Zvara, I.: Radiochim. Acta **46**, 113 (1989).
- [57] Türlér, A.: Radiochim. Acta, accepted for publication (1995).
- [58] Kadkhodayan, B., Türlér, A., Gregorich, K.E., Nurmia, M.J., Lee, D.M., Hoffman, D.C.: Nucl. Instrum. Methods in Phys. Res. **A317**, 254 (1992).
- [59] Gäggeler, H.W., Jost, D., Kovacs, J., Scherer, U.W., Weber, A., Vermeulen, D., Türlér, A., Gregorich, K.E., Henderson, R.A., Czerwinski, K.R., Kadkhodayan, B., Lee, D.M., Nurmia, M.J., Hoffman, D.C., Kratz, J.V., Goyer, M.K., Zimmermann, H.P., Schädel, M., Bröchle, W., Schimpf, E., and Zvara, I.: Radiochim. Acta **57**, 93 (1992).
- [60] Türlér, A., Gäggeler, H.W., Gregorich, K.E., Barth, H., Bröchle, W., Czerwinski, K.R., Goyer, M.K., Hannink, N.J., Henderson, R.A., Hoffman, D.C., Jost, D.T., Kacher, C.D., Kadkhodayan, B., Kovacs, J., Kratz, J.V., Kreek, S.A., Lee, D.M., Leyba, J.D., Nurmia, M.J., Schädel, M., Scherer, U.W., Schimpf, E., Vermeulen, D., Weber, A., Zimmermann, H.P., Zvara, I.: J. Radioanal. Nucl. Chem. **160**, 327 (1992).
- [61] Eichler, B., Türlér, A., Jost, D.T., Gäggeler, H.W.: Annual Report 1993, Labor für Radio- und Umweltchemie, Paul Scherrer Institut (1994), p.42.

- [62] Türlér, A., Jost, D.T., Piguet, D., Eichler, B., Mendel, M., Nähler, A., Eberhardt, K., Trautmann, N.: Annual Report 1994, Labor für Radio- und Umweltchemie, Paul Scherrer Institut (1995), p.43.
- [63] Hoffman, D.C., Lee, D.M., Ghiorso, A., Nurmia, M.J., Aleklett, K., Leino, M.: Phys. Rev. C **24**, 495 (1981).
- [64] Jost, D.T., Vermeulen, D.: IEEE, Trans. Nucl. Sci. **39**, 186 (1992).
- [65] Czerwinski, K.R., Gregorich, K.E., Hannink, N.J., Kacher, C.D., Kadkhodayan, B., Kreek, S.A., Lee, D.M., Nurmia, M.J., Türlér, A., Seaborg, G.T., Hoffman, D.C.: Radiochim. Acta **64**, 23 (1994).
- [66] Czerwinski, K.R., Kacher, C.D., Gregorich, K.E., Hamilton, T.M., Hannink, N.J., Kadkhodayan, B., Kreek, S.A., Lee, D.M., Nurmia, M.J., Türlér, A., Seaborg, G.T., Hoffman, D.C.: Radiochim. Acta **64**, 29 (1994).
- [67] Schädel, M., Brüchle, W., Jäger, E., Schimpf, E., Kratz, J.V., Scherer, U.W., Zimmermann, H.P.: Radiochim. Acta **48**, 171 (1989).
- [68] Kratz, J.V., Zimmermann, H.P., Scherer, U.W., Schädel, M., Brüchle, W., Gregorich, K.E., Gannet, C.M., Hall, H.L., Henderson, R.A., Lee, D.M., Leyba, J.D., Nurmia, M.J., Hoffman, D.C., Gäggeler, H., Jost, D., Baltensperger, U., Ya Nai-Qi, Türlér, A., Lienert, Ch.: Radiochim. Acta **48**, 121 (1989).
- [69] Goyer, M.K., Kratz, J.V., Zimmermann, H.P., Schädel, M., Brüchle, W., Schimpf, E., Gregorich, K.E., Türlér, Hannink, N.J., Czerwinski, K.R., Kadkhodayan, B., Lee, D.M., Nurmia, M.J., and Hoffman, D.C., Gäggeler, H., Jost, D., Kovacs, J. Scherer, U.W., Weber, A.: Radiochim. Acta **57**, 77 (1992).
- [70] Zimmermann, H.P., Goyer, M.K., Kratz, J.V., Schädel, M., Brüchle, W., Schimpf, E., Gregorich, K.E., Türlér, Czerwinski, K.R., Hannink, N.J., Kadkhodayan, B., Lee, D.M., Nurmia, M.J., and Hoffman, D.C., Gäggeler, H., Jost, D., Kovacs, J. Scherer, U.W., Weber, A.: Radiochim. Acta **60**, 11 (1993).
- [71] Bruchertseifer, H., Eichler, B., Estevez, J., Zvara, I.: Radiochim. Acta **47**, 41 (1989).
- [72] Szegłowski, Z., Bruchertseifer, H., Domanov, V.P., Gleisberg, B., Guseva, L.J., Hussonnois, M., Tikhomirova, G.S., Zvara, I., Oganessian Yu.Ts.: Radiochim. Acta **51**, 71 (1990), and Radiokhimiya **33**, 90 (1991).
- [73] Persson, H., Skarnemark, G., Skålberg, M., Alstad, J., Liljenzin, J.O., Bauer, G., Haberberger, F., Kaffrell, N., Rogowski, J., Trautmann, N.: Radiochim. Acta **48**, 177 (1989), and Alstad, J., Skarnemark, G., Haberberger, F., Herrmann, G., Nähler, A., Pense-Maskow, M., Trautmann, N.: J. Radioanal. Nucl. Chem. **189**, 133 (1995).

- [74] Wierczinski, B., Eberhardt, K., Herrmann, G., Kratz, J.V., Mendel, M., Nähler, A., Rocker, F., Tharun, U., Trautmann, N., Weiner, K., Wiehl, N., Alstad, J., Skarnemark, G.: Nucl. Instrum. Methods A, submitted for publication (1995).
- [75] Eberhardt, K., Alstad, J., Eichler, B., Gäggeler, H.W., Herrmann, G., Jost, D.T., Kling, H.O., Mendel, M., Nähler, A., Piguet, D., Skarnemark, G., Tharun, U., Trautmann, N., Türlér, A., Weiner, K., Wiehl, N.: Institut für Kernchemie, Univ. Mainz, Jahresbericht 1994, IKMz 95-1 (1995) p.11.
- [76] Gregorich, K., Wierczinski, B., Mendel, M., Nähler, A., Alstad, J., Skarnemark, G.: private communication 1995.
- [77] Schädel, M., for a Darmstadt-Mainz-Göteborg-Oslo-Villigen- Bern-Dresden-Leipzig-Kassel-Berkeley-collaboration: UNILAC-proposal *Studies of Element 106 Properties*, GSI Darmstadt 1994.
- [78] Malli, G.L. (ed.): *Relativistic and Electron Correlation Effects in Molecules and Solids*, NATO ASI Series Vol. 318, Plenum Press, New York (1994).
- [79] Pershina, V.: Chem. Rev., accepted for publication (1995).
- [80] Fricke, B., Waber, J.T.: Actinides Rev. **1**, 433 (1971).
- [81] Fricke, B., 1975, In: *Structure and Bonding*, eds. Dunitz, J.D., et al., Vol. 21, Springer Verlag, Berlin, pp. 90-142.
- [82] Desclaux, J.P.: At. Data Nucl. Data Tables **12**, 311 (1973).
- [83] Desclaux, J.P., Freeman, A.J.: In: *Handbook on the Physics and Chemistry of the Actinides*, eds. Freeman A.J., Lander, G.H., North-Holland, Amsterdam (1984) p.1-77.
- [84] Glebov, V.A., Kasztura, L., Nefedov, V.S., Zhuikov, B.L.: Radiochim. Acta **46**, 117 (1989).
- [85] Zhuikov, B.L., Glebov, V.A., Nefedov, V.S., Zvara, I.: J. Radioanal. Nucl. Chem. **143**, 103 (1990).
- [86] Johnson, E. Fricke, B., Keller, O.L.Jr., Nestor, C.W., Tucker, T.C.: J. Chem. Phys. **93**, 8041 (1990).
- [87] Fricke, B., Johnson, E., Rivera, G.M.: Radiochim. Acta **62**, 17 (1993).
- [88] Eliav, E., Kaldor, U., Ishikawa, Y.: Phys. Rev. Letters **74**, 1079 (1995).
- [89] Rosen, A., Ellis, D.E.: J. Chem. Phys. **96**, 3039 (1975).
- [90] Pershina, V., Sepp, W.D., Fricke, B., Rosen, A.: J. Chem. Phys. **96**, 8367 (1992).

- [91] Pershina, V., Sepp, W.D., Fricke, B., Kolb, D., Schädel, M., Ionova, G.V.: J. Chem. Phys. **97**, 1116 (1992).
- [92] Pershina, V., Sepp, W.D., Bastug, T., Fricke, B., Ionova, G.V.: J. Chem. Phys. **97**, 1123 (1992).
- [93] Pershina, V., Fricke, B.: J. Phys. Chem. **98**, 6468 (1994).
- [94] Eichler, B.: Annual Report 1993, Labor für Radio- und Umweltchemie, Paul Scherrer Institut (1994), p.38.
- [95] Eichler, B., Türlér, A., Gägglér, H.W.: Annual Report 1994, Labor für Radio- und Umweltchemie, Paul Scherrer Institut (1995), p.34 and p.35.
- [96] Desclaux, J.P., Fricke, B.: J. Phys. **41**, 943 (1980)
- [97] Brewer, L.: High Temp. Sci. **17**, 1 (1984)
- [98] Ryzhkov, M.V., Gubanov, V.A., Zvara I.: Radiochim. Acta **57**, 11 (1992).
- [99] Türlér, A., Gägglér, H.W., Eichler, B., Jost, D.T., Kovacs, J., Scherer, U.W., Kadkhodayan, B., Gregorich, K.E., Hoffman, D.C., Kreek, S.A., Lee, D.M., Schädel, M., Brüchle, W., Schimpf, E., Kratz, J.V.: Proc. School Seminar on Heavy Ion Physics, Dubna, May 1993, and Paul Scherrer Institut Rep. PSI-PR-93-12, 1993.
- [100] Eichler, B., Zvara, I.: Radiochim. Acta **30**, 233 (1982).
- [101] Jost, D.T., Gägglér, H.W., Vogel, Ch., Schädel, M., Jäger, E., Eichler, B., Gregorich, K.E., Hoffman, D.C.: Inorg. Chim. Acta **146**, 255 (1988).
- [102] Eichler, B., Hübener, S., Gägglér, H.W., Jost, D.T.: Inorg. Chim. Acta **146**, 162 (1988).
- [103] Czerwinski, K.R.: *Studies of Fundamental Properties of Rutherfordium (Element 104) Using Organic Complexing Agents*, Ph.D. Thesis, Berkeley (1992); Rep. **LBL-32233** (1992).
- [104] Pershina, V., Fricke, B.: J. Chem. Phys. **99**, 9720 (1993).
- [105] Pyykkö, P.: Chem. Rev. **88**, 563 (1988).
- [106] Ionova, G.V., Pershina, V., Johnson, E., Fricke, B., Schädel, M.: J. Chem. Phys. **96**, 11096 (1992).
- [107] Scherer, U.W., Kratz, J.V., Schädel, M., Brüchle, W., Gregorich, K.E., Henderson, R.A., Lee, D.M., Nurmia, M.J., Hoffman, D.C.: Inorg. Chim. Acta **146**, 249 (1988).

- [108] Pershina, V., Fricke, B., Kratz, J.V., Ionova, G.V.: *Radiochim. Acta* **64**, 37 (1994).
- [109] Hyde, E.K., Hoffman, D.C., Keller, O.L.Jr.: *Radiochim. Acta* **42**, 57 (1987).
- [110] Kadkhodayan, B.: *On-Line Gas Chromatographic Studies of Rutherfordium (Element 104), Hahnium (Element 105), and Homologs*, Ph.D. Thesis, Berkeley (1993); Rep. **LBL-33961** (1993).
- [111] Eliav, E., Kaldor, U., Schwerdtfeger, P., Hess, B.A., Ishikawa, Y.: *Phys. Rev. Letters* **73**, 3203 (1994).
- [112] Pershina, V., Fricke, B.: *J. Phys. Chem.* **99**, 144 (1995).
- [113] Zvara, I.: contribution to the Third Int. Conf. on Nuclear and Radiochemistry, Wien, September 7-12, 1992, and Timokhin, S.N., Zvara, I.: private communications.
- [114] Schädel, M., Jäger, E., Schimpf, E., Bröchle, W.: *Radiochim. Acta* **68**, 1 (1995).
- [115] Schädel, M., Jäger, E., Bröchle, W., Sümmerer, K., Hulet, E.K., Wild, J.F., Loughheed, R.W., Moody, K.J.: *Radiochim. Acta* **68**, 7 (1995).

Figure Captions

Fig. 1. Periodic Table of the Elements. While in group 3 the chemistry of all lanthanides follows quite uniformly that of their prototype element lanthanum such a behaviour is found only for the second half of the actinides. The arrangement of the actinides reflects that the first actinide elements still resemble, to a decreasing extent, the chemistry of the other groups: Th the fourth group below Hf, Pa the fifth group below Ta, U the sixth group below W, Np the seventh group below Re, and Pu the eighth group below Os. The known transactinide elements 104 through 111 shall take the positions below Hf in group 4 and Au in group 11.

Fig. 2. Schematic representation of the target and recoil-chamber arrangement in transactinide chemistry experiments. Fig. from [60,28]

Fig. 3. Schematic of the on-line isothermal gas chemistry set-ups OLGA II and HEVI coupled to two alternative detection devices for α -spectroscopy and SF-fragment kinetic-energy measurements, a tape system and a rotating wheel. Fig. from [57]).

Fig. 4. Photograph of the computer-controlled Automated Rapid Chemistry Apparatus, ARCA II [67]. See text for description.

Fig. 5. a) Thermochromatographically determined deposition zone of element 104 chlorides (black dots) and Hf (solid line) compared with Sc (dashed line) and heavy actinides (open circles). b) Temperature gradient in the column. From [13].

Fig. 6. Gas-chromatographically determined relative chemical yield for Zr (open circles), Hf (triangles) and Rf (solid squares) chlorides as a function of the temperature in the isothermal part of the column together with Monte Carlo simulations (solid line). Inserted in the figure are the chlorinating gases used and the deduced adsorption enthalpies [99]. Figure from [57].

Fig. 7. Extraction of ^{261}Rf , ^{95}Zr , ^{169}Hf , ^{228}Th , and ^{238}Pu into 0.25 M TBP in benzene as a function of chloride concentration. The H^+ concentration was kept constant at 8 M. Adapted from [66].

Fig. 8. a) (upper panel) Distribution of fission tracks (circles) attributed to element 105 bromides from three thermochromatographic experiments compared with the ^{90}Nb distribution, and the temperature gradient along the column. b) (lower panel) Measured integral distribution of 14.6-h ^{90}Nb and 3.3-min ^{169}Hf (smooth solid lines) are compared to the measured integral fission distribution (dashed step function), and a calculated region (dashed area) which compensates for the short half-life of 1.8-s ^{261}Ha . Adapted from [17].

Fig. 9. Relative yield of Nb (triangles), Ta (solid dots) and Ha (squares) bromides as a function of the temperature in the isothermal part of the gas-chromatography column [59,51]. Inserted in the figure are the brominating agents and the deduced adsorption enthalpies which were used for the Monte-Carlo Simulations (solid lines). Figure from [51].

Fig. 10. Vapor pressure curves for Nb, Ta, and Ha bromides. The curve HaBr_5 exp. was deduced from the experimental data shown in Fig. 9. The curve theor.-rel. is from [91] and the area denoted theor.-non-rel. from [94]. Figure from [51].

Fig. 11. Relative yield of NbCl_5 (dots) and NbOCl_3 (diamonds) in comparison with the relative yield of HaCl_5 and HaOCl_3 (triangles) as a function of the temperature in the isothermal part of the gas-chromatography column [57]. The solid lines are from Monte Carlo simulations with the adsorption enthalpies given in the figure. Figure from [57].

Fig. 12. Diagram of elution curves for trivalent actinides (An), Nb, Ta, and Pa from TIOA columns (1.6 mm x 8 mm), under the same conditions as in the Ha experiments. The inserts show the relative amount of element 105 found in each specific eluent. Figure from [27] adapted from [68].

Fig. 13. Fractional extracted activity of Ta, Nb, and Pa tracers (curves) as a function of HCl concentration in the system TIOA – HCl/0.03 M HF. The bold bars encompass the upper and lower limits deduced for the Ha extraction from the elution positions in the chromatography experiments, see text. The bar for the complete extraction of Ha from 12 M HCl/0.02 M HF is not included in the figure for clarity. Figure from [28] adapted from [70].

1		2												18																								
H 1		He 2																																				
3		4												10		17		18																				
Li		Be																		F		Ne																
11		12												18		17		18																				
Na		Mg																		Cl		Ar																
19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36				
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr				
37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54				
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe				
55		56		57		72		73		74		75		76		77		78		79		80		81		82		83		84		85		86				
Cs		Ba		La*		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn				
87		88		89		104		105		106		107		108		109		110		111																		
Fr		Ra		Ac+		Rf/Ku		Ha		Sg		Ns		Hs		Mt																						

*** Lanthanides**

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig.5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13