

# Gas chemical properties of heaviest elements

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*Transactinides / Gas phase / Chemical properties*

**Summary.** Chemical studies at the upper end of the periodic table have reached atomic number 114. Recent experiments aiming at investigating chemical properties of elements Cn, 113, and 114 are summarized. Though partly preliminary, all these elements behave as expected: due to the filled  $6d^{10}$  shell, they do not behave like transition metals anymore, as observed for the lighter transactinides. They exhibit a volatile behavior as expected for  $7s$  and  $7p$  elements. On the other hand, due to the extremely low signal to noise ratio in detectors used to identify separated products highest precaution on identifying single atoms is mandatory. As an example, published early attempts to synthesize Cn and to perform chemical studies with this element that could not be confirmed in later studies are summarized.

## 1. Introduction

Chemical studies of transactinides reach back to the 1960<sup>th</sup> [1]. From the very beginning gas phase techniques have been successfully applied to investigate properties of the lighter transactinides, the  $6d$ -elements Rf, Db, Sg, and Bh. The compounds studied most extensively were the volatile chlorides and bromides – also in form of their oxohalides. Typical temperatures at which the chromatographic studies were performed ranged from 150 °C to 400 °C because these compounds are volatile at these temperatures (see *e.g.* [2]). For Hs, a member of group 8, the best suited volatile molecule is the tetroxide. This was the first time gas chemical studies had to be performed in cryo-chromatographic setups [3] due to the very high volatility of  $\text{HsO}_4$ . Chemical studies on the heavier  $6d$  elements Mt, Ds, and Rg are still missing. Several review articles and monographs summarize these early gas chemical investigations [2, 4–6].

Heaviest elements are a test ground for chemistry and the periodic table: are the basic principles of Mendeleev still valid or have deviations to be expected due to relativistic effects [7]. Such effects are predicted to influence electronic orbital energies and, hence, chemical properties with increasing atomic number: due to strong Coulomb forces between the highly charged nuclei and orbiting electrons their velocities increase to values close to the speed of light – even for valence electrons. This causes a relativistic mass increase. As a consequence, a shrinking of the average radii

of spherical  $s$  and  $p_{1/2}$  orbital's result (direct relativistic effect). Energies of these orbital's increase. Due to resulting shielding effects high angular momentum orbital's ( $p_{3/2}$ , all  $d$  and  $f$  orbital's) are destabilized (indirect relativistic effect) which lower their energies [8].

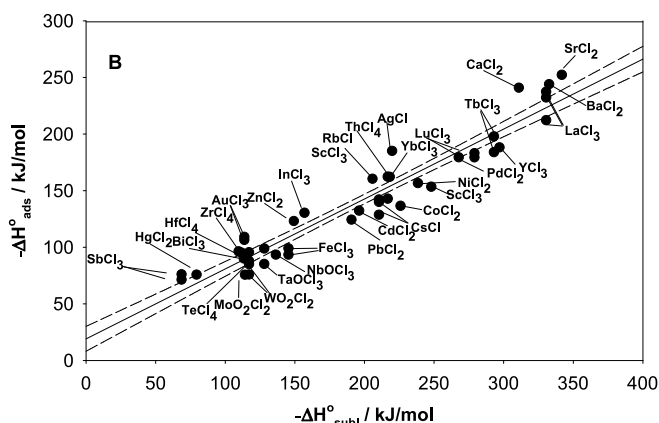
Of special interest are spin-orbit effects, becoming very pronounced as a consequence of such relativistic effects. Exceptionally high spin-orbit splitting is expected for the  $p$  orbital's since the  $p_{1/2}$  orbital is stabilized (spherical) while the  $p_{3/2}$  orbital is destabilized (distorted). For the heaviest transactinides currently under investigation (Cn and above) the  $6d$  shell is complete and the  $7s$  and  $7p$  electrons are being filled in. For *e.g.* element 114 ( $[\text{Rn}]7s^26d^{10}7p^2$ ) the energy difference between the filled  $7p_{1/2}$  and empty  $7p_{3/2}$  orbital's amounts to about 4 eV, which makes this element a candidate for a very noble and volatile behavior [9]. This means that in contrast to the lightest member of group 14 to which element 114 belongs, carbon, Hund's rule does not apply anymore.

The determination of the volatility (or sublimation enthalpy as a measure of the volatility) of a new element is truly a challenge, because in the strict sense the term volatility is defined for macro amounts. Usually solid-state properties such as *e.g.* the cohesive energy is a measure of the volatility. This value encounters the energy required to separate a single atom from a bulk of atoms assembled in a well defined crystal structure.

The drawbacks of experiments with transactinides are that they can be produced only at a single-atom-at-a-time level. This prevents any study of macro chemical properties. The only feasible way to deduce information on macro chemical properties is to use proxies which empirically correlate micro chemical observables with macro chemical properties. As has been extensively shown, highly significant linear correlations exist between adsorption enthalpies of given classes of chemical compounds (chlorides, bromides, oxides, elements) of micro amounts on a given chromatographic surface with their respective thermochemical properties such as *e.g.* sublimation enthalpy or boiling point, *i.e.*  $-\Delta H_{\text{ads}}^\circ \propto \Delta H_{\text{subl}}^\circ$ . It is then assumed – though not proven – that such correlations also describe the relation between micro and macro properties of new elements or their compounds, respectively. One examples of such a correlation is depicted in Fig. 1 for chlorides and oxochlorides on quartz surfaces.

Favourable to gas chemical studies is the fact that appropriate chromatographic setups can be easily coupled to

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**Fig. 1.** Correlation of adsorption enthalpies of single atoms or molecules on quartz surfaces with their sublimation enthalpy for chlorides and oxochlorides. The linear correlation is  $-\Delta H_{\text{ads}}^{\circ} = (21.5 \pm 5.2) + (0.600 \pm 0.025) \cdot \Delta H_{\text{subl}}^{\circ}$  (from [10]).

accelerators (see *e.g.* [11, 12]). This enables continuous and fast separation of products. Usually, a collection chamber is positioned behind a fixed target or a rotating target wheel where products formed in complete fusion reactions with high recoil energy are collected in a carrier gas (mostly helium or helium/argon mixtures). Via continuous gas flow collected atoms are then transported through thin capillaries to chromatographic devices. In more recent years it became advantageous to not couple the collection chamber directly behind a target station but behind a physical separator which itself is coupled to a target station at a beamline. This approach was pioneered at Lawrence Berkeley National Laboratory where such a physical separator was operated in form of a gas-filled magnet (BGS separator) [13]. In the focal plane of BGS a septum in form of a thin and gastight Mylar foil separates the gas-filled magnet kept at low gas-pressure from the collecting chamber with the flowing transport gas kept at ambient pressure. The success of this novel technique motivated other chemistry groups to also develop this technique such as at GSI with TASCA, at FLNR with DGFRS, or at RIKEN with GARIS.

Another stringent constraint for chemical investigation of heaviest elements is the availability of isotopes with sufficiently long half-lives. The fastest chemical investigations performed up to now need approx. one second separation time. This means that elements are accessible to chemical investigation if isotopes with half-lives of approx. 0.5 s or longer are known.

To extract reliable chemical information from the observation of few atoms multiple interactions usually of gas-solid type is required in gas chromatography columns. Chemisorption or physisorption processes define the interaction time of a given species with the surface of a chromatographic tube. This interaction process is analysed as function of temperature, since the interaction time  $\tau$  is strongly depending on this parameter *via* the Frenkel equation:

$$\tau = \tau_0 e^{-Q/RT}$$

with  $Q$  being the interaction energy between the gaseous atom (or molecule) and the surface material,  $R$  the gas constant and  $T$  the temperature.  $\tau_0$  is a constant. In real ex-

periments single atoms are subjected to up to  $10^5$  interactions [14]. In single atom chemistry reaction rates have to be quantified on the basis of statistical probabilities, derived from the chemical equations, but coupled to Monte Carlo models in order to predict trajectories of individual species in a given system (see *e.g.* [14]).

Currently, chemical experiments with the heaviest elements are conducted at large heavy ion accelerators in Dubna, Russia, at the Flerov Laboratory for Nuclear Reactions (FLNR), in Darmstadt, Germany, at the Helmholtz Centre Gesellschaft für Schwerionenforschung (GSI) and in Wako-Shi, Saitaman, Japan at RIKEN. The most successful pathway to produce heaviest elements is to fuse  $^{48}\text{Ca}$  projectiles with actinide targets such as  $^{238}\text{U}$ ,  $^{242/244}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{245,248}\text{Cm}$ ,  $^{249}\text{Bk}$ , or  $^{249}\text{Cf}$ , respectively. At energies close to the fusion barrier, as a result of the reaction  $Q$ -value, compound nuclei are formed with 30 to 40 MeV excitation energy. This means that three to four prompt neutrons are emitted prior to reaching the final evaporation residue. The lighter transactinides Rf to Hs were synthesized in more asymmetric reactions that lead to compound nuclei with somewhat higher excitation energies of 40 to 50 MeV. Typical reactions used for chemical studies were  $^{18}\text{O} + ^{248}\text{Cm}$  for synthesis of Rf,  $^{18}\text{O} + ^{249}\text{Bk}$  for Db,  $^{22}\text{Ne} + ^{248}\text{Cm}$  for Sg,  $^{22}\text{Ne} + ^{249}\text{Bk}$  for Bh, and  $^{26}\text{Mg} + ^{248}\text{Cm}$  for Hs, respectively (see *e.g.* [15]).

This manuscript concentrates on the recent gas chemical experiments with Cn, element 113 and 114. For extensive overviews on our current understanding of the chemical properties of lighter transactinides we refer to review articles (*e.g.* [15]). Some emphasis will first be given to unsuccessful attempts to study Cn, both its nuclear physical properties as well as its chemical behavior. This example exemplifies the sometimes painful meander, experimental scientists have to follow prior to reaching the final goal. Indeed, experiments with heaviest transactinides are truly a search for the needle in a haystack!

## 2. Early – most likely – misinterpreted experiments with copernicium

Since many decades it was generally accepted that most suited for synthesis of elements above Rg is to bombard an actinide target with a  $^{48}\text{Ca}$  beam. Already back in the middle of the 1970<sup>th</sup> search experiments were conducted both at FLNR in Dubna and at LBNL in Berkeley using this strategy [16, 17]. Later, this approach was tried again several times with novel experimental setups that enabled search experiments with improved sensitivity [18]. All these bombardments failed: no indication for the existence of any nuclide in the region of transactinides (so-called superheavy elements) was observed. It remained unclear whether this was a lack of experimental sensitivity or a mere failure of predicted stability of existing nuclei in this region of the chart of nuclides (for review, see [19]).

In the 1990<sup>th</sup> FLNR developed a vacuum in-flight separator designed as an energy filter (VASSILISSA) to be applied in the field of heaviest element synthesis and detection. To the very big surprise, in 1999 a collaboration of scientists from Russia, Germany, Slovakia and Japan announced the observation of two spontaneous fission (SF) events in the

detector array mounted in the focal plane during a bombardment of  $^{238}\text{U}$  with  $^{48}\text{Ca}$  [20]. These two SF events were tentatively assigned to  $^{283}\text{Cn}$  formed in a complete fusion reaction followed by emission of three neutrons. From the measured life times (time between implantation signal in the detector and measured SF decay) a half-life for  $^{283}\text{Cn}$  of  $81_{-32}^{+147}$  s could be deduced. A later identical experiment performed by the same collaboration yielded again two SF events with on average a half-life of 9.5 min. Also these two events were ascribed to  $^{283}\text{Cn}$  [21]. This was the first claimed observation of an evaporation residue in a reaction between  $^{48}\text{Ca}$  and an actinide target. Even more surprising was the exceptional long half-life. The result was met with some criticism due to the long correlation time between implantation signal and radioactive decay at a none negligible background count rate in the detector array [22].

In order to confirm the surprising observation two additional experiments were suggested. First, a physics experiment using the reaction  $^{48}\text{Ca} + ^{242}\text{Pu}$  which should form  $^{287}114$  and then  $^{283}\text{Cn}$  after emission of a  $\alpha$ -particle and, second, a chemistry experiment.

In the physics experiment again using the VASSILISSA separator two  $\alpha$ -SF decay chains were detected which were ascribed to the decay of  $^{287}114$ . The  $\alpha$ -energies of the two decaying atoms of  $^{287}114$  were 10.29 MeV and 2.31 MeV (escape  $\alpha$ ). The consecutive SF-decays happened 9.3 min and 3.8 min later, in good agreement with the expected decay of  $^{283}\text{Cn}$  from the experiments with the  $^{238}\text{U}$  target. This remarkable result was published by a Russian, German, Italian, Slovakian, Japanese collaboration in the high-ranking journal Nature [23].

A several-minute half-life isotope of Cn should make a chemical investigation rather easy. Even more, because predictions claim Cn to behave like a very volatile noble metal if not like a noble gas. This prediction emerges from a straightforward extrapolation of volatilities of  $p$ -elements (see Fig. 2 from [24]).

As in the physics experiments, in this first chemical study the nuclide  $^{283}\text{Cn}$  was synthesized by bombarding a  $2\text{ mg/cm}^2$  thick  $^{238}\text{U}$  target with a center of the target (cot) beam energy of 233 MeV  $^{48}\text{Ca}$  ions. In a first chemistry experiment performed by a Russian, German collaboration, a chemical similarity between Cn and Hg was assumed. Therefore, simultaneously, short-lived Hg isotopes were produced from a small admixture of Nd to the target material that enables chemical control of the experiment with the nearest by homologue of Cn. In test experiments short-lived Hg isotopes could be isolated in elemental form from other reaction products and transported in a He carrier gas flow quantitatively through a 30 m long Teflon<sup>TM</sup> capillary at room temperature. Hg adsorbs quantitatively at room temperature on noble metal surfaces such as Au, Pt, and Pd surfaces. Eight detector chambers (6 Au and 2 Pd) were connected in series by Teflon tubing. The detector chambers were positioned inside an assembly of 84  $^3\text{He}$  filled neutron detectors (in a polyethylen moderator) in order to simultaneously detect neutrons accompanying spontaneous fission events (Fig. 3). During the bombardment a total beam dose of  $6.85 \times 10^{17}$   $^{48}\text{Ca}$  ions was accumulated [25]. The chemical yield for the simultaneously produced  $^{185}\text{Hg}$  ( $T_{1/2} = 49$  s) was 80% and the average trans-

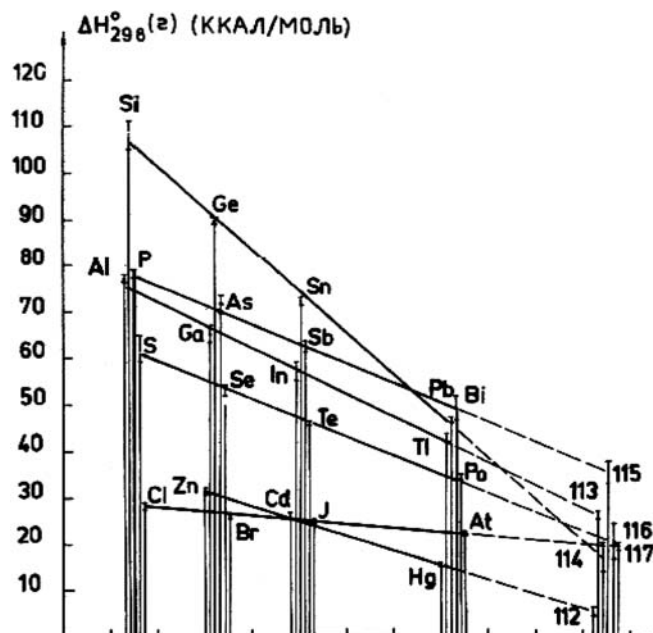


Fig. 2. Formation enthalpy of gaseous elements in kcal/mole (resembling sublimation enthalpies) within groups of the periodic table that lead to the transactinides 112 to 117 (from [24]).

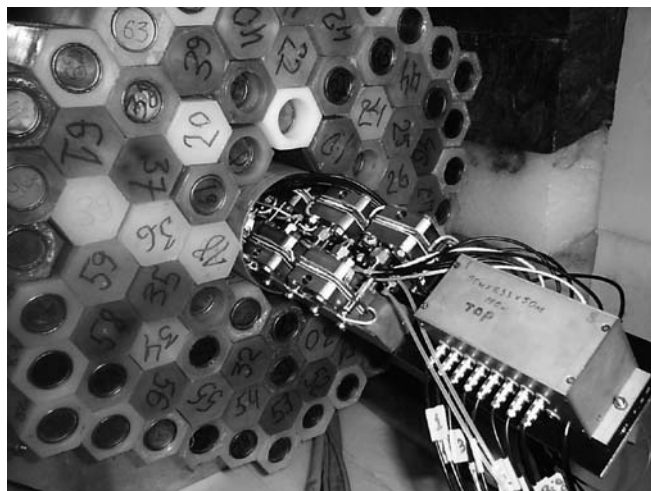


Fig. 3. Detector arrangement for the detection of  $^{283}112$  consisting of pairs of Au and Pd coated PIPS detectors inside an assembly of 84  $^3\text{He}$  filled neutron detectors. Photograph reproduced from [25].

port time between collection chamber and detector array 25 s. If Cn behaves chemically like Hg and all efficiencies measured for Hg were also valid for Cn, detection of SF events could be expected assuming the cross section value for the production of  $^{283}\text{Cn}$  measured in [20, 21]. However, no SF events were observed. Therefore, the experiment was interpreted as indication for a non-Hg like behavior of Cn.

In a next experiment, the question whether Cn remained in the gas phase and passed over the Au and Pd surfaces was addressed. Therefore, a gas ionization chamber to measure SF fragments of nuclei remaining in the gas was added at the exit of the detector array. A total beam dose of  $2.8 \times 10^{18}$   $^{48}\text{Ca}$  ions was accumulated on an identical  $^{238}\text{U}$  target during an experiment performed by a Russian, Swiss, German, Polish collaboration [26]. Again zero SF events were registered on the Au and Pd coated PIPS detectors, confirming



the result of the first experiment. However, eight high energy events accompanied by up to three neutrons were registered in the ionization chamber, while only one background count was expected. These single energy events were attributed to the SF-decay of an isotope of Cn, since there are no other known volatile nuclides decaying by SF, even though they could not be assigned to fission fragment coincidences. It was argued that the fissioning nuclides were deposited on surfaces inside the ionization chamber causing a situation where only detection of single fission fragment energies was possible. Therefore, the authors state that “the spontaneous fissions of the volatile activity can be conclusively attributed to the decay of element 112 (now Cn) produced in the reaction  $^{48}\text{Ca} + ^{238}\text{U}$ , and formerly observed in Dubna physics experiments” [20, 21].

From this second chemistry experiment it appears that the interaction of Cn with an Au or Pd surface is much weaker than for Hg. The deduced enthalpies of adsorption were  $-\Delta H_a^0(\text{Hg}) \geq 75 \text{ kJ/mol}$  and  $-\Delta H_a^0(\text{Cn}) \leq 55 \text{ kJ/mol}$ . It was concluded that such a vastly different chemical behavior as in the present case of Cn compared to its lighter homologue Hg has not been observed for any of the lighter transactinides so far and was interpreted as being caused by relativistic effects. It was suggested, that a next experiment should focus on a measurement of the adsorption enthalpy of Cn on Au surfaces in a cryo-chromatographic device.

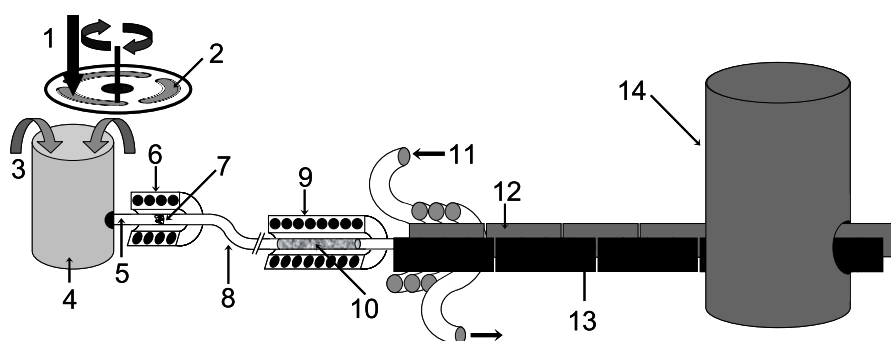
Such a device was previously developed and applied for the first chemical investigation of Hs [27]. In a collection chamber behind the target recoiling hassium atoms (radicals) were *in-situ* oxidized to  $\text{HsO}_4$  by adding some oxygen to the He carrier gas and heating the products to  $800^\circ\text{C}$ . Since  $\text{HsO}_4$  is a gaseous molecule at room temperature semiconductor detectors were arranged inside of a thermochromatographic column and operated between  $-20^\circ\text{C}$  and  $-170^\circ\text{C}$ . This set-up was named IVO (*in-situ* volatilization and on-line detection) [3].

For the experiment with copernicium the same device was applied with some modification: one side of the chromatographic column consisted of  $32 \text{ } 1 \times 1 \text{ cm}^2$  active area PIN diodes, while the opposite side consisted of a Au covered plate ( $2\pi$  counting geometry only) (Fig. 4). The temperature gradient covered inside of the detector array was between  $+35^\circ\text{C}$  and  $-184^\circ\text{C}$ , respectively. As reported at a conference by a collaboration from Switzerland, Ger-

many, USA, China, and Russia, during a bombardment of a  $1.5 \text{ mg/cm}^2$  thick  $^{238}\text{U}$  target with a  $^{48}\text{Ca}$  beam (cot-beam energy =  $239 \text{ MeV}$ , beam dose =  $2.8 \times 10^{18}$ ) seven high energy events ( $E \geq 40 \text{ MeV}$ ) were detected at various temperatures, three out of the seven being observed at very low temperatures where Rn was deposited [28]. These events, however, were too low in energy to correspond to fission fragments. It was argued, that due formation of a thin layer of ice on the surface of the detectors below about  $-95^\circ\text{C}$  (as seen by the reduced  $\alpha$ -resolution of the spectra), the measured energies were originating from SF fragments after some energy loss in the ice layer. Also, the seven events resembled a production cross section of a few picobarn, in good agreement with observations from the previous experiments. Therefore, these events were assigned to the presumable SF decay of  $^{283}\text{Cn}$ . Hence, the result of this experiment was interpreted to be in full support of the first chemical experiment [26].

All six publications, three from physics experiments [20, 21, 23] and three from chemistry experiments [25, 26, 28] yielded a consistent picture, namely that Cn has a very long-lived isotope,  $^{283}\text{Cn}$  with a half-life of several minutes and that Cn behaves very similar to a noble gas like Rn, hence significantly different to its nearest-by neighbor in the periodic table, Hg.

Later experiments, both in independent physics and chemistry experiments at different laboratories turned out to be in conflict with all observations described in this chapter! First, physics experiments conducted at FLNR with another on-line separator, the Dubna gas-filled separator (DGFRS) was unable to confirm the observations made at the VASSILISSA separator in the same reaction and at identical bombarding energy. Instead, as main product of the reaction  $^{48}\text{Ca}$  on  $^{238}\text{U}$  a  $\alpha$ -decaying product was observed with a half-life of about  $4 \text{ s}$  [29]. This decay was assigned to  $^{283}\text{Cn}$ , in clear conflict with the earlier observation. In a second experiment  $^{242}\text{Pu}$  was bombarded with  $^{48}\text{Ca}$ , keeping all the parameters identical to the previous VASSILISSA experiment. But now, a  $\alpha$ -decay chain was detected interpreted to start with  $^{287}114$  ( $E_\alpha = 10.02 \text{ MeV}$ ) and decaying after  $0.5 \text{ s}$  to  $^{283}\text{Cn}$  that decayed again *via*  $\alpha$ -emission, in agreement with the result of the previous study [29]. Later physics experiments at LBNL (using the reaction  $^{48}\text{Ca}$  on  $^{242}\text{Pu}$ ) [30] as well as at GSI using the reaction  $^{48}\text{Ca}$  on



**Fig. 4.** IVO (*in-situ* volatilisation and on-line detection) device used for the first thermochromatographic study of Cn. Beam (1) impinging on a rotating target wheel (2). He carrier gas (3) flushing the recoil chamber (4). Quartz tube (5) connecting the collection chamber with a aerosol collecting quartz wool plug (7) inside of an oven (6). PFA capillary (8) connecting oven (7) with a getter oven (9) filled with heated Ta and Ti foils (10). Detector array with  $\text{H}_2\text{O}$  cooling on the entrance side (11) and liquid nitrogen cooling on the other (14). Au covered metal plates (12) and  $32 \text{ } 1 \times 1 \text{ cm}^2$  size PIN detectors (13).

$^{238}\text{U}$  [31] supported the interpretation that  $^{283}\text{Cn}$  is a  $\alpha$ -decaying isotope with a half-life of about 4 s and not a SF decaying isotope with a half-life of several minutes.

This situation asked for a new series of chemical investigation of Cn with improved setups that enable separation of nuclides in the few-second range (see below).

What remains is an explanation of all these misinterpreted bombardments. Without entering a detailed discussion here it turns out that interpretation of physical or chemical observables on the basis of detected high energy events, ascribed to be from SF decays is very problematic. It is, however, worth mentioning that the life times of the SF decay's observed in the physics experiments increased from experiment to experiment. In [20] the two observed SF events had an average life time of 2.0 min, in [23] 6.6 min, and, finally, in [21] 13.7 min. This mere fact indicates the events being of random origin, with an "effective" increase in life time being caused by increasingly improved separation properties of the VASSILISSA separator from experiment to experiment. In the chemistry experiments the interpretation of the events is even more problematic since no SF coincidences were observed in both attempts and the measured single energy signals were clearly lower than expected [26, 28]. Hence, the possibilities to misinterpret these events are manifold (scattered beam, secondary particles such as *e.g.* neutrons or muons entering the detection volume *etc.*).

### 3. Chemical studies with copernicium

The IVO set-up [3] had to be improved in three main parameters: counting geometry, transportation time and purity from traces of water vapor inside the array. The counting set-up was increased from a  $2\pi$  to a  $4\pi$  geometry (as was already the case in the Hs experiments). Both sides inside the detector array were  $32\ 1 \times 1\ \text{cm}^2$  silicon detectors, one side being covered by a about 50 nanometer thin Au layer. This enabled detection of  $\alpha$ -decay chains with high efficiency and SF events *via* detection of coincident fission fragments. The transportation time was significantly reduced from about 30 s to 4 s (and in later experiments stepwise to 2 and fi-

nally to 1 s) *via* reducing the length of the transport capillary between collection chamber at the accelerator and the chromatography set-up. Moreover, the device was operated in a loop mode to reduce the water vapor content of the carrier gas. The IVO device used for the Cn experiments and the experiments with element 114 is depicted in Fig. 5.

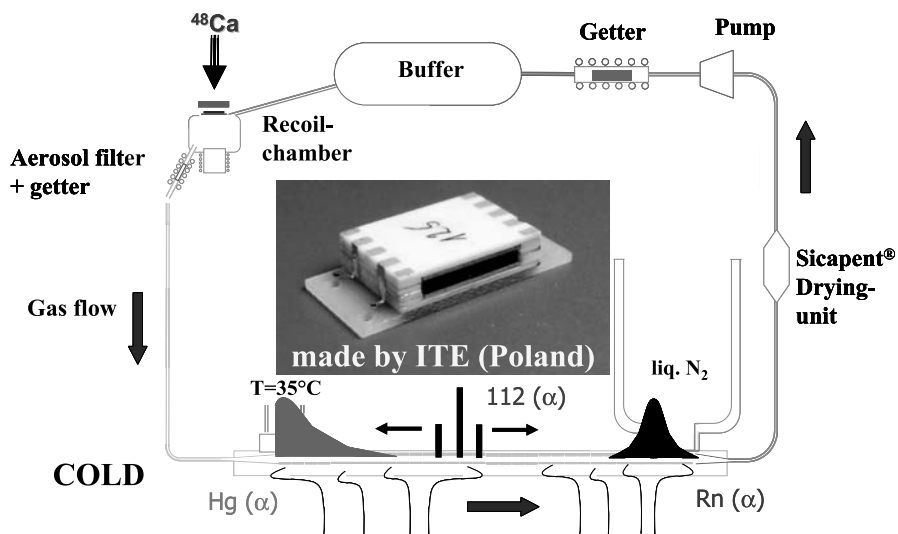
In two experiments using the  $^{48}\text{Ca} + ^{238}\text{U}$  ( $1.6\ \text{mg}/\text{cm}^2$ ) reaction at cot-beam energies of 231 and 234 MeV, respectively, with a total beam dose of  $5.9 \times 10^{18}$ , no event was observed that could be ascribed  $^{283}\text{Cn}$  [33]. The cross section limit reached was 1.3 pb. This sensitivity was interpreted as insufficient to be in disagreement with physics experiments which produced  $^{283}\text{Cn}$  in this reaction with – on average – 1.5 pb [29, 31].

As an ultimate choice an attempt was made to try investigating the chemical properties of Cn by using a reaction that first produces element 114. The reason for this rather unusual strategy was the observation that production cross sections increase when going from Cn to element 114 using the  $^{48}\text{Ca}$  induced reactions [34]. A prerequisite of this approach is, however, that first an isotope of element 114 is formed that has a too short half-life for chemical study, followed by an isotope of Cn with a sufficiently long half-life. The ideal case that fulfills this requirement is the reaction  $^{48}\text{Ca} + ^{242}\text{Pu}$ . The decay chain observed in physics experiments using this reaction is depicted in Fig. 6.

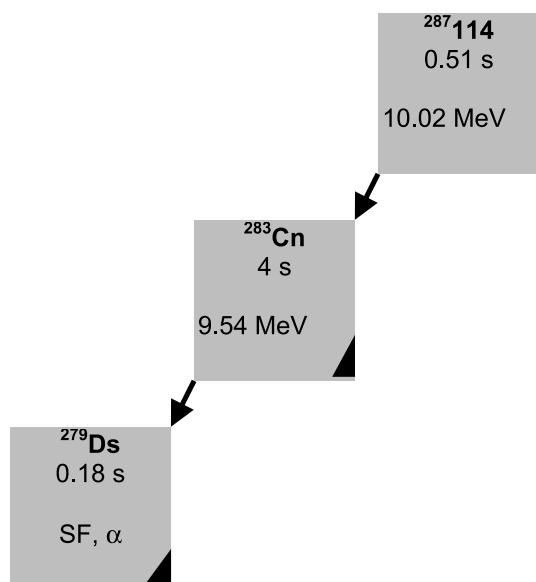
With a transport time of 2.2 s between collection chamber and detection array the yield of element 114 is reduced to 5% while for Cn it reaches 68%. In the course of two bombardments of a  $1.4\ \text{mg}/\text{cm}^2$  thick  $^{242}\text{Pu}$  target with a  $^{48}\text{Ca}$  cot-beam energy of 236 MeV five decay chains were detected starting with  $^{283}\text{Cn}$  followed by SF-decays within less than one second [32, 35] (Fig. 7). Since no signal can be detected upon deposition of an atom on the surface of the detector, no information may be gained about the half-life of the first decaying product. However, with a transport time of about 2 s a minimum value on the order of seconds is plausible.

The deposition positions of the five atoms inside of the detector array are depicted in Fig. 8.

The resulting value for the adsorption enthalpy of Cn on the Au surface of  $-52\ \text{kJ}/\text{mole}$  is in good agreement with



**Fig. 5.** IVO device used for the experiments with Cn and element 114. The unit is operated in a closed-loop mode to enable highest possible purification from water vapor and from trace contaminants. The detector array consisted of  $32\ 1 \times 1\ \text{cm}$  silicon detector pairs (see insert) along which a stationary temperature gradient was established. One side of the detector pairs were covered by a thin Au layer (modified from [32]).



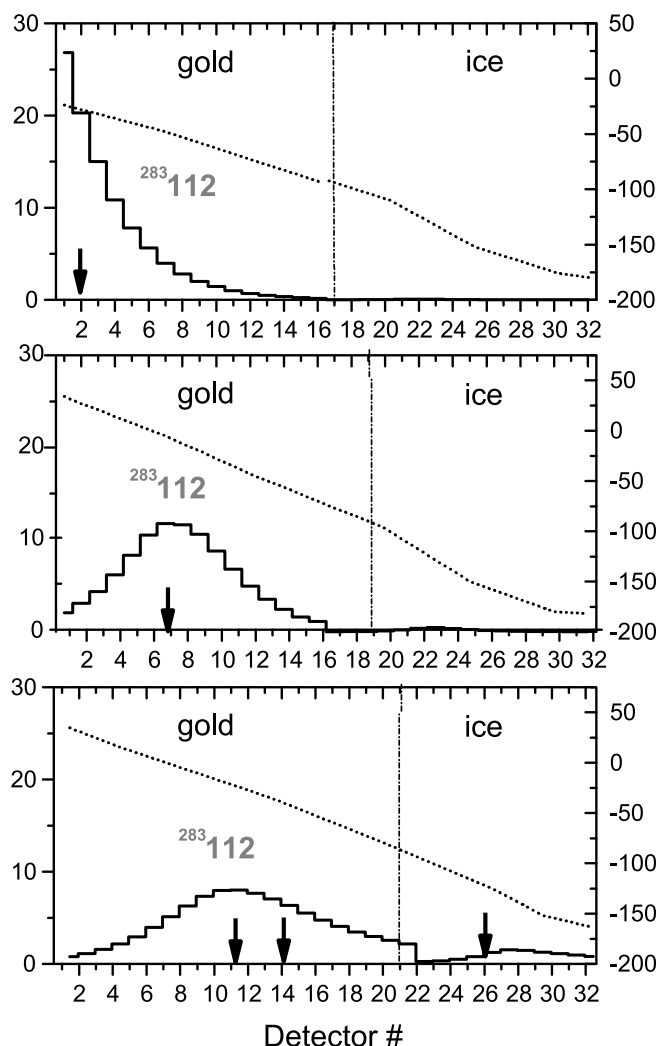
**Fig. 6.** Decay chain observed in the reaction  $^{48}\text{Ca} + ^{242}\text{Pu}$  [29, 34] and used for the first chemical experiment with Cn.

a theoretical prediction that yielded 44 kJ/mole applying fully relativistic four-component functional theory calculation [48].

One additional atom of Cn was detected in a bombardment conducted later using the same reaction and beam parameters as described above ( $^{242}\text{Pu}$  target thickness 1.4 mg/cm<sup>2</sup>, beam dose  $3.4 \times 10^{18}$ ,  $^{48}\text{Ca}$  cot-beam energy 235 MeV). The isotope  $^{283}\text{Cn}$  decayed at a temperature in the detector array of  $-7^\circ\text{C}$  by emission of a 9.3 MeV  $\alpha$  particle followed by a SF decay 73 ms later, in agreement with the data depicted in Fig. 8 [36].

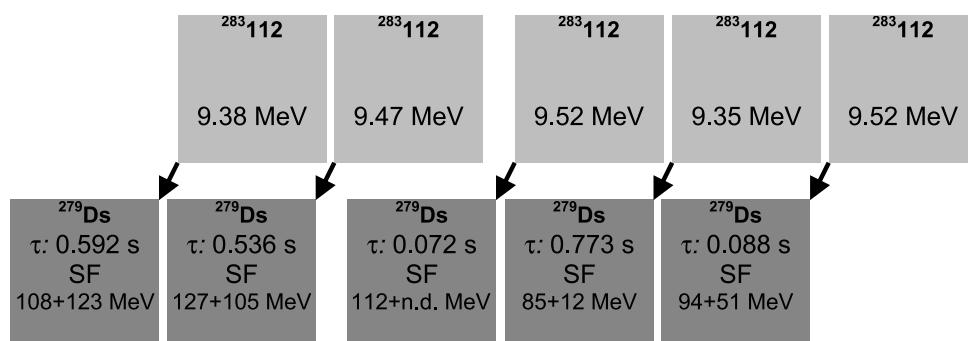
In order to gain information on the volatility of Cn a proxy was established between adsorption enthalpies of *s*- and *p*-elements and of some noble gases on Au surfaces and their respective sublimation enthalpies (similar to the example depicted in Fig. 1), see Fig. 9 [37].

Taking the correlation depicted in Fig. 9 a sublimation enthalpy for Cn of  $\Delta H_{\text{subl}} = 39^{+23}_{-10}$  kJ/mole ( $= 4.8^{+2.8}_{-1.2}$  kcal/mole) results, in excellent agreement with the classical estimate from Fig. 2, but somewhat lower than theoretically expected from calculated solid state properties of Cn (110 kJ/mole [38]). Hence, copernicium is a very volatile noble metal, still resembling much its neighbor in group 12, Hg, but being more volatile. It can not be fully excluded that Cn in macro amounts is a gas at standard conditions (predicted boiling point between 249 and 469 K) [35]. It

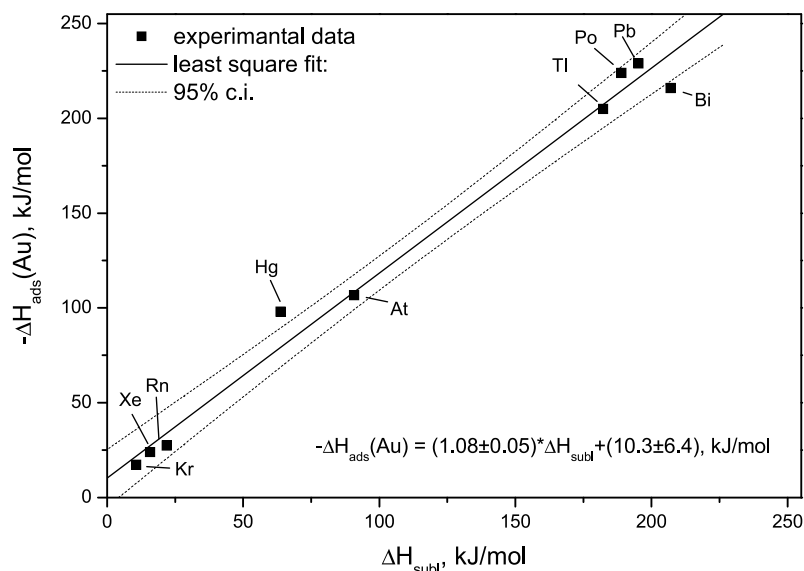


**Fig. 8.** Deposition of the five detected atoms (indicated by arrows) assigned to  $^{283}\text{Cn}$  in the two  $^{48}\text{Ca} + ^{242}\text{Pu}$  experiments. The dotted lines indicate the temperature gradient inside the detector array (right axis in  $^\circ\text{C}$ ). Three different regimes in term of temperature range inside of the detector array and gas flow rates were applied. The solid lines depict results of a Monte Carlo model prediction (left axis in rel. yield) including the given experimental parameters and assuming the deposited atoms to have always an adsorption enthalpy with the Au surface of  $-52$  kJ/mole [14]. The vertical dashed lines at detectors 17, 19, and 21, respectively, indicates the start of ice layer formation towards lower temperatures as clearly seen in reduced resolutions in the  $\alpha$ -spectra (from [35]).

should be mentioned, however, that the correlation depicted in Fig. 9 used as proxy a linear correlation connecting microchemical adsorption enthalpies with macrochemical sub-



**Fig. 7.** Decay chains observed in the experiments to study the chemical property of Cn (from [35]).



**Fig. 9.** Correlation between measured microchemical adsorption enthalpies on Au surfaces of homologues of elements Cn through 118 and their respective sublimation enthalpy (from [37]).

limation enthalpies. This approach is questioned by some authors. [39].

One additional atom of Cn was detected in a follow-up experiment using the reaction  $^{48}\text{Ca} + ^{244}\text{Pu}$  reaction (target thickness  $0.44 \text{ mg/cm}^2$ , cot-beam energy  $244 \text{ MeV}$ ) behind the Dubna gas-filled magnetic separator. In this bombardment one decay chain  $^{285}\text{Cn}$  ( $E_\alpha = 9.15 \text{ MeV}$ )  $\rightarrow$   $^{281}\text{Ds}$  ( $\text{SF}_{\text{coinc.}}$  after  $3.4 \text{ s}$ ) was detected at  $-93^\circ\text{C}$  [40], within chemical resolution still in agreement with previous observation for Cn (see Fig. 8). This novel strategy in chemistry studies with heaviest elements to “pre-clean” the spectrum of products formed in nucleon transfer reactions from the wanted few atoms from complete fusion turned out to be very successful. This approach is actually also pursued at GSI with the TASCA gas-filled magnetic separator [41] for study of the chemical property of element 114 [42].

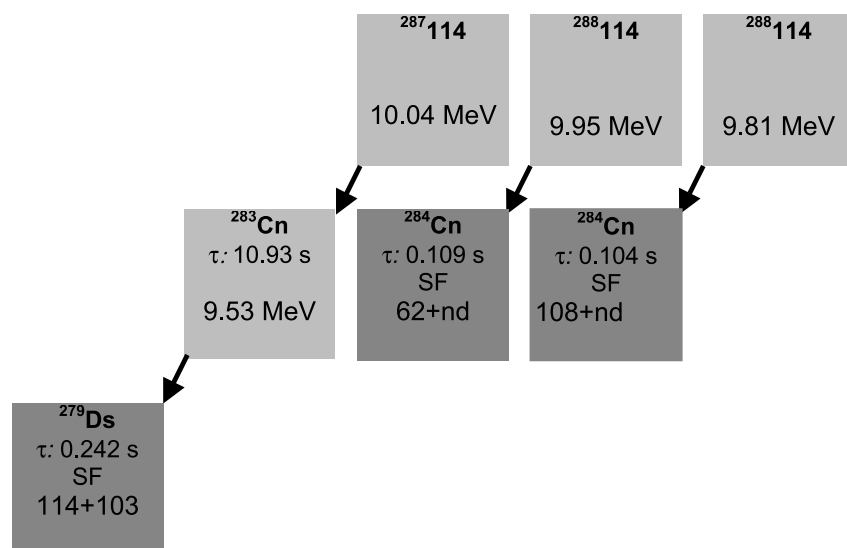
#### 4. Chemical studies with element 114

Expectations predict for element 114 a lower volatility than for Cn (see Fig. 2 but also more recent predictions

[7, 39, 43, 44]). It was therefore highly questionable whether element 114 would be transported in elemental form through the transport capillary kept at room temperature which connects the recoil chamber with the detector array. As a rule of thumb it is known from experimental observation that single atoms of Hg are well transported through such capillaries while *e.g.* At is transported only partially. Fig. 2 depicts element 114 to lie in its volatility between these two elements.

To the big surprise, during the experiments with Cn using the  $^{48}\text{Ca} + ^{242}\text{Pu}$  reaction, one decay chain was observed that could be assigned to the decay of  $^{287}\text{114}$  (Fig. 10; left chain). The probability that this observed chain is not from a decay of an atom of element 114 but from Cn (first  $\alpha$  particle being of random origin) was calculated to be 2% [45]. This surprising observation, given the yield reduction of  $^{287}\text{114}$  during the transport down to 5% and the observation of its deposition temperature inside of the detector array at  $-94^\circ\text{C}$  clearly asked for additional experiments.

Therefore, new experiments were conducted, now with the reaction  $^{48}\text{Ca} + ^{244}\text{Pu}$ . The reason for the change in the target material was the observation that longer-lived isotopes



**Fig. 10.** Decay chains observed in the experiments to study element 114 in the reactions  $^{48}\text{Ca} + ^{242}\text{Pu}$  (left chain) and  $^{244}\text{Pu}$  (middle and right chains). The members of the right chain were observed in different detectors (see [45]).  $\tau$  is the life time. The probabilities to be of random origin are 2% for the left chain (only first to second  $\alpha$ ) and 0.15 and 1.1%, respectively, for the other chains (from [45]). The SF energies are in MeV.

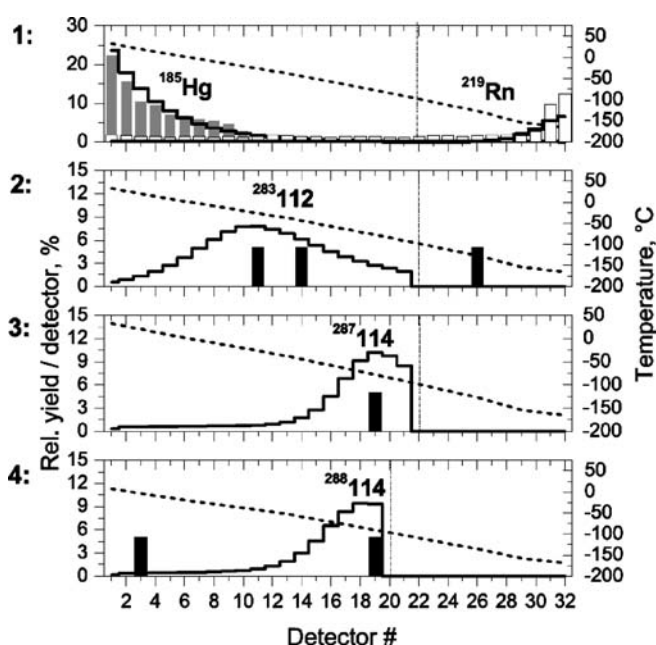


of element 114 are formed in this reaction,  $^{288}\text{114}$  ( $T_{1/2} = 0.7\text{ s}$ ) and  $^{289}\text{114}$  ( $T_{1/2} = 2.1\text{ s}$ ) (combined value from [34] and [46]).

During a bombardment of a  $1.4\text{ mg/cm}^2$  thick  $^{244}\text{Pu}$  target with  $4.5 \times 10^{18}$   $^{48}\text{Ca}$  particles (cot-beam energy  $242\text{ MeV}$ ) two event chains were detected that could be assigned to  $^{288}\text{114}$  (Fig. 10; middle and right chains) [45]. Some additional decay chains were detected as candidates for the decay of the longer-lived isotope  $^{289}\text{114}$ , however, at a random rate that surmounted the number of observed chains. Therefore these decay chains had to be discarded.

The deposition pattern of the three atoms of element 114 inside the detector array is depicted in Fig. 11, together with three atoms of Cn that were observed during the same bombardments (see above). The solid lines depict Monte Carlo predictions assuming that the atom of element 114 observed at  $-7^\circ\text{C}$  is from a decay during the transport [14, 47]. This yields an adsorption enthalpy for element 114 on Au of  $34^{+20}_{-3}\text{ kJ/mole}$  [45]. However, as is evident from Fig. 11, the chromatographic resolution inside the column at the experimental high gas velocities is very poor (see Monte Carlo distribution for Cn). In other words, the number of theoretical plates in the chromatography column is very low. Hence, all three deposited atoms of element 114 would still fit inside the distribution of Cn. Therefore, with the actual accuracy of the scarce data it is not possible to deduce any statement on the volatility sequence between Cn and element 114, both seem to behave rather similarly.

On the basis of the proxy depicted in Fig. 9 the resulting sublimation enthalpy of element 114 amounts to  $23^{+22}_{-8}\text{ kJ/mole}$ , again within error identical to the value for Cn.



**Fig. 11.** Deposition pattern inside of the detector array for Hg and Rn (top), of three atoms of Cn observed in the  $^{242}\text{Pu}$  bombardment (second), of the single atom of element 114 detected in the  $^{242}\text{Pu}$  bombardment (third), and of the two atoms of element 114 found in the  $^{244}\text{Pu}$  bombardment (fourth) (for details see text). The dashed lines indicate the temperature gradient inside the detector array. The bold solid lines depict the Monte Carlo model predictions. The vertical thin lines depict the onset of ice formation towards lower temperatures.

The sequence in adsorption enthalpies (being indirectly proportional to the volatility) that emerges from the experiments with Cn [32, 35] and element 114 [45], as well as additional measurements with Hg and Pb yielded  $\text{Pb} > \text{Hg} > \text{Cn} \geq 114$ , in disagreement with a theoretical prediction that resulted in  $\text{Pb} > 114 > \text{Hg} > \text{Cn}$  [48]. However, a recent calculation of solid-state properties of group 14 elements that includes spin-orbit effects yielded a very low cohesive energy (= sublimation enthalpy) for element 114 due to the very large energy gap of about  $4\text{ eV}$  between the filled  $7p_{1/2}$  and the empty  $7p_{3/2}$  sub-shells [49]. The predicted cohesive energy for element 114 was  $0.45\text{ eV}$ , in reasonable agreement with the experimental value of  $0.23^{+0.22}_{-0.08}\text{ eV}$  [45].

Very recently, an experiment has been conducted at improved chemical conditions behind TASCA to investigate the chemical properties of element 114 using the same  $^{48}\text{Ca} + ^{244}\text{Pu}$  reaction [42, 50] (target thickness  $0.44\text{ mg/cm}^2$ , beam dose  $0.98 \times 10^{18}$ , cot-beam energy  $243.8\text{ MeV}$ ). In these experiments an isothermal Au covered detector array was positioned prior to the detector array along which a negative temperature gradient was established. Two events ascribed to atoms of element 114 were detected inside of the isothermal column kept at room temperature and one atom assigned to Cn in the thermochromatographic detector array [50]. The data analysis of this bombardment is in progress. This observation yields indication for a behavior of element 114 being sufficiently volatile to be transported through a capillary to a detector array.

## 5. Ongoing chemical studies with element 113

The discovery experiments at FLNR of the elements 115 using the reaction  $^{48}\text{Ca} + ^{243}\text{Am}$  [34] and of element 117 using  $^{48}\text{Ca} + ^{249}\text{Bk}$  [51] yielded access to isotopes of element 113 (as decay products) with sufficiently long half-lives for chemical study. In case of the  $^{48}\text{Ca} + ^{243}\text{Am}$  synthesis of predominantly  $^{288}\text{115}$ , the decay chain passes through  $^{284}\text{113}$  with a half-life of  $0.5\text{ s}$  and in  $^{48}\text{Ca} + ^{249}\text{Bk}$  of predominantly  $^{293}\text{117}$  via  $^{286}\text{113}$  with a half-life of several seconds, respectively. The discovery claim of element 115 [34] was corroborated by an experiment that isolated a decay product of the decay chain by chemical means [52].

As is evident from Fig. 2, but also pointed out in [39] for element 113 an even lower volatility is expected compared to the volatilities of Cn and of element 114. Despite this expectation a chemical experiment was designed using a very similar setup as applied previously for the studies of Cn and element 114. The only modifications were to operate the Au covered detector array at a constant temperature of  $0^\circ\text{C}$  and to heat a shortest possible transport capillary of  $2\text{ m}$  length between collection chamber and detector array to  $70^\circ\text{C}$ . This enabled to achieve a minimum transport time of  $0.8\text{ s}$  at a gas flow rate of  $3\text{ L/min}$  [53]. During two bombardments of a  $1.0\text{ mg/cm}^2$  thick  $^{243}\text{Am}$  with a total beam dose of  $4.7 \times 10^{18}$  no  $\alpha$ -decay chains were observed that could be assigned to the decay of  $^{284}\text{113}$  [53]. In a second experiment, a  $1.6\text{ mg/cm}^2$  thick  $^{249}\text{Bk}$  target was bombarded with  $9.1 \times 10^{18}$   $^{48}\text{Ca}$  particles. Indeed, in the detector array two candidates for decay chains from  $^{286}\text{113}$  were observed [54]. It is premature to interpret this observation as an indication



of a high volatility for element 113 in its elemental state. It is conceivable that this element forms a hydroxide with trace amounts of oxygen and/or water vapor in the system which – if element 113 behaves similarly to Tl – is expected to be more volatile than the elemental state [53, 55].

## 6. Concluding remarks

The last decade has opened up fascinating new perspectives for gas chemical studies of heaviest elements. This became possible thanks to the discovery of several isotopes of elements up to atomic number 118 (eka-Rn) in  $^{48}\text{Ca}$  induced fusion reactions with actinides targets [34, 51]. This situation stimulated, in a first round, chemical studies of Cn and element 114. All information gained so far point to a highly volatile behavior of both elements, even though the sequence in volatility between the two elements remains open. On-going are studies of element 113 where it remains unclear, what chemical species is being investigated in the current bombardments.

The actual limit for chemical investigation is limited to isotopes with half-lives of approx. 0.5 s or longer. This limit was reached in the observation of  $^{287,288}\text{114}$  [45]. From early unsuccessful experiments with Cn it became evident that chemical experiments with heaviest elements are conducted at the limit of current technology. Often, one event per week of bombardment has to be identified with high probability not to be of random origin. Hence, utmost care has to be taken to interpret detected signals with highest precaution. In that respect, future chemical investigation in this field will largely benefit from the “pre-cleaning” strategy *via* placing a physical separator between the target and a chemical device. The lower production rates (*e.g.* due to thinner targets that can be used) is largely overcompensated by the significantly improved reduction of background signals in the detector arrays.

Future steps in chemical studies could be i) to try to reach the current ultimate limit with element 115, *e.g.* by using  $^{290}\text{115}$  ( $T_{1/2} = 0.7$  s) from the  $^{48}\text{Ca} + ^{249}\text{Bk}$  reaction, ii) trying to fill the gap between Hs and Cn with first chemical studies of Mt and Rg where sufficiently long isotopes for chemical investigation that decay *via* emission of  $\alpha$ -particles are accessible in the reactions  $^{48}\text{Ca} + ^{249}\text{Bk}$  or  $^{243}\text{Am}$ , respectively. Ds remains a problem as no  $\alpha$ -decaying isotope with  $T_{1/2} \geq 0.5$  s is known yet. Finally, iii) to confirm the extremely long-lived neutron-rich isotopes claimed to exist as final members of some of the decay chains observed in Dubna that have half-lives of up to one day for the trans-actinides Rf and Db [34, 51, 52]. Such neutron-rich isotopes might be accessible in nucleon transfer reactions, separated on-line with the future IRIS separator at GSI [56].

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