

Recent achievements in chemical studies of heaviest elements

H W Gäggeler

Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Abstract. Discovery of heavy elements up to atomic number 118 at FLNR in Dubna has paved the way to also extend chemical knowledge to heavier members of the periodic table. Recent studies on the chemical properties of Cn and element 114 are summarized that have been performed at FLNR in Dubna using the fusion reactions $^{48}\text{Ca} + ^{242/244}\text{Pu}$.

Email: Heinz.gaeggeler@psi.ch

1. Introduction

The recent discovery of several elements up to atomic number 118 in ^{48}Ca induced fusion reactions at the Flerov Laboratory for Nuclear Reactions (FLNR) in Dubna (see e.g. [1]) paved the way to extend also the chemical knowledge to heavier members of the periodic table. 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 [2]. 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 [3].

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 behaviour [4].

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.

Favourable to gas chemical studies is the fact that appropriate chromatographic setups can be easily coupled to accelerators (see e.g. [5]). 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.

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 τ 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. τ_0 is a constant. In real experiments single atoms are subjected to up to 10^5 interactions. 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. [6]).

This manuscript concentrates on the recent gas chemical experiments with Cn, and element 114 conducted at FLNR.

2. Chemical studies with copernicium

The In-situ Volatilisation and On-line detection system IVO) [7] used for these experiments is depicted in Figure 1. Reaction products were collected in a recoil chamber flushed with a He/Ar mixture. Stopped products were then transported through a thin PFA capillary (1.6 mm dia.) to a counting device, consisting of 32 $1 \times 1 \text{ cm}^2$ Si detector pairs mounted opposite to each other at a distance of 1.5 mm (see Figure 1). One side of the detectors being covered by a about 50 nanometer thin Au layer. Along the detector array a stationary negative temperature gradient was established (+35 to – 170 °C). This enabled detection of α -decay chains with high efficiency and SF events via detection of coincident fission fragments. In two experiments using the $^{48}\text{Ca} + ^{238}\text{U}$ (1.6 mg/cm²) reaction at center-of-target (cot) beam energies of 231 and 234 MeV, respectively, with a total beam dose of 5.9×10^{18} , no event was observed that could be ascribed ^{283}Cn [9] that decays with a half life of 4 s (see Figure 2).. 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}Cn in this reaction with – on average – 1.5 pb [10,11].

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}Ca induced reactions [1]. 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 Figure 2.

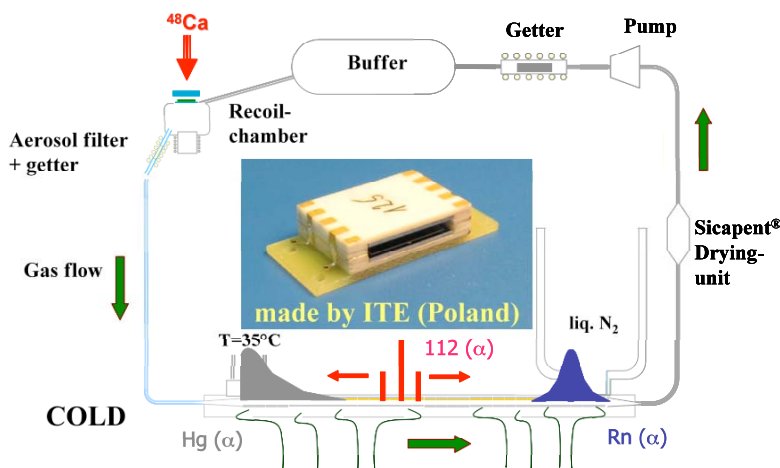


Figure 1. IVO device used for the experiments with Cn and element 114. The unit is operated in a closed-loop mode to enable highest possible purification from water vapour and from trace contaminants. The detector array consisted of 32 1x1 cm silicon detector pairs (see insert) along which a stationary temperature gradient was established. One side of the detector pairs were covered by a thin Au layer (modified from [8]). Detection efficiencies were 82 % for α -particles, 63 % for fission coincidences and 37 % for single fission fragments if atoms adsorbed on the active Au surface inside the detector array [18].

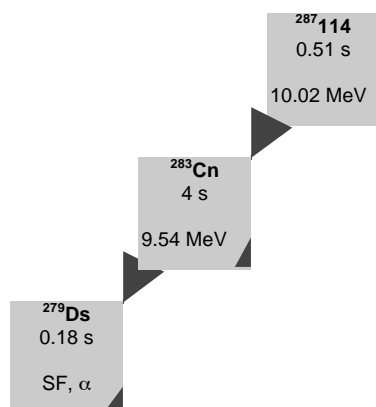


Figure 2. Decay chain observed in the reaction $^{48}\text{Ca} + ^{242}\text{Pu}$ [1,10] and used for the first chemical experiment with Cn.

With a transport time of 2.2 s in this experiment 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 mg/cm² thick ^{242}Pu target with a ^{48}Ca cot-beam energy of 236 MeV five decay chains were detected starting with ^{283}Cn followed by SF-decays within less than one second [8, 12] (Figure 3). 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 Figure 4. The value for the adsorption enthalpy of Cn on the Au surface of -52 kJ/mole is in good agreement with a

theoretical prediction that yielded 44 kJ/mole applying fully relativistic four-component functional theory calculation [13].

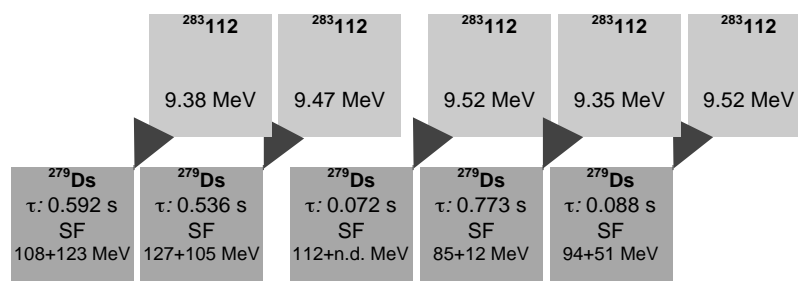


Figure 3. Decay chains observed in the experiments to study the chemical property of Cn (from [12]). n.d.: not detected.

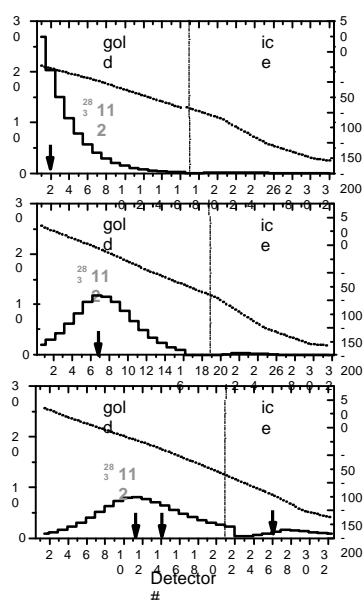


Figure 4. Deposition of the five detected atoms (indicated by arrows) assigned to ^{283}Cn in the two $^{48}\text{Ca} + ^{242}\text{Pu}$ experiments. The dotted lines indicate the temperature gradient inside the detector array (right axis in $^{\circ}\text{C}$). Three different regimes in term of temperature 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 [6]. 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 α -spectra.

One additional atom of Cn was detected in a bombardment conducted later using the same reaction and beam parameters as described above (^{242}Pu target thickness 1.4 mg/cm², beam dose 3.4×10^{18} , ^{48}Ca cot-beam energy 235 MeV). The isotope ^{283}Cn decayed at a temperature in the detector array of -7 $^{\circ}\text{C}$ by emission of a 9.3 MeV α particle followed by a SF decay 73 ms later, in agreement with the data depicted in Figures 3 and 4 [14].

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, see Figure 5 [15].

Taking the correlation depicted in Figure 5 a sublimation enthalpy for Cn of $\Delta H_{\text{subl}} = 39^{+23}_{-10}$ kJ/mole (= $4.8^{+2.8}_{-1.2}$ kcal/mole) results, somewhat lower than theoretically expected from calculated solid state properties of Cn (110 kJ/mole [16]). Hence, copernicium is a very volatile noble metal, still resembling much its neighbour 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) [12].

3. Chemical studies with element 114

Expectations predict for element 114 a lower volatility than for Cn (see e.g. [17]). 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.

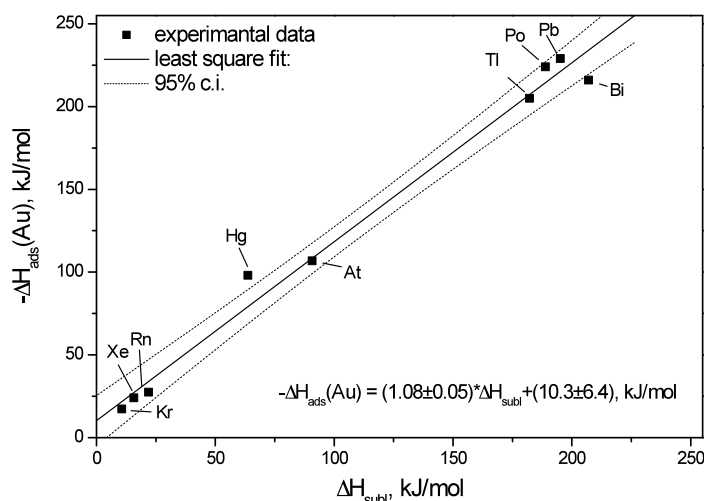


Figure 5. Correlation between measured microchemical adsorption enthalpies on Au surfaces of homologues of elements Cn through 118 and their respective sublimation enthalpy (from [15]).

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 287114 (Figure 6; left chain). The probability that this observed chain is not from a decay of an atom of element 114 but from Cn (first a particle being of random origin) was calculated to be 2 % [18]. This surprising observation, given the yield reduction of 287114 during the transport down to 5 % and the observation of its deposition temperature inside of the detector array at -94°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 of element 114 are formed in this reaction, 288114 ($T_{1/2} = 0.7\text{s}$) and 289114 ($T_{1/2} = 2.1\text{s}$) (combined value from [1] and [19]).

During a bombardment of a 1.4 mg/cm^2 thick 244Pu target with 4.5×10^{18} 48Ca particles (cot-beam energy 242 MeV) two event chains were detected that could be assigned to 288114 (Figure 6; middle and right chains) [18]. Some additional decay chains were detected as candidates for the decay of the longer-lived isotope 289114 , however, at a random rate that surmounted the number of observed chains. These decay chains had therefore to be discarded.

The deposition pattern of the three atoms of element 114 inside the detector array is depicted in Figure 7, 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°C is from a decay during the transport [6, 18]. This yields an adsorption enthalpy for element 114 on Au of $34 \pm 20 \pm 3\text{ kJ/mole}$ [18]. However, as is evident from Figure 7, the chromatographic resolution inside the column at the experimental high gas velocities is very poor (see Monte Carlo distribution for Cn). 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 Figure 5 the resulting sublimation enthalpy of element 114 amounts to $23 \pm 22 \pm 8\text{ kJ/mole}$, again within error identical to the value for Cn.

The sequence in adsorption enthalpies (being indirectly proportional to the volatility) that emerges from the experiments with Cn and element 114, 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 $\text{Pb} > 114 > \text{Hg} > \text{Cn}$ [13]. 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 eV between the filled 7p_{1/2} and the empty 7p_{3/2} sub-shells [20]. The predicted cohesive energy for element 114 was 0.45 eV, in reasonable agreement with the experimental value of 0.23+0.22-0.08 eV [18].

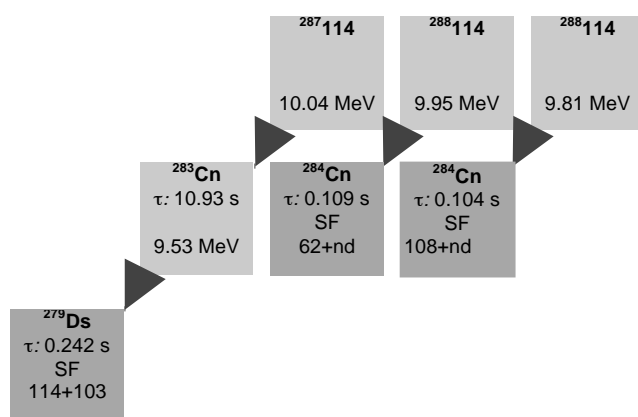


Figure 6. Decay chains observed in the experiments to study element 114 in the reactions $^{48}\text{Ca} + ^{242}\text{Pu}$ (left chain) and ^{244}Pu (middle and right chains). The members of the right chain were observed in different detectors (see [18]). τ is the life time. The probabilities to be of random origin are 2 % for the left chain (only first to second α) and 0.15 and 1.1 %, respectively, for the other chains (from [18]). The SF energies are in MeV.

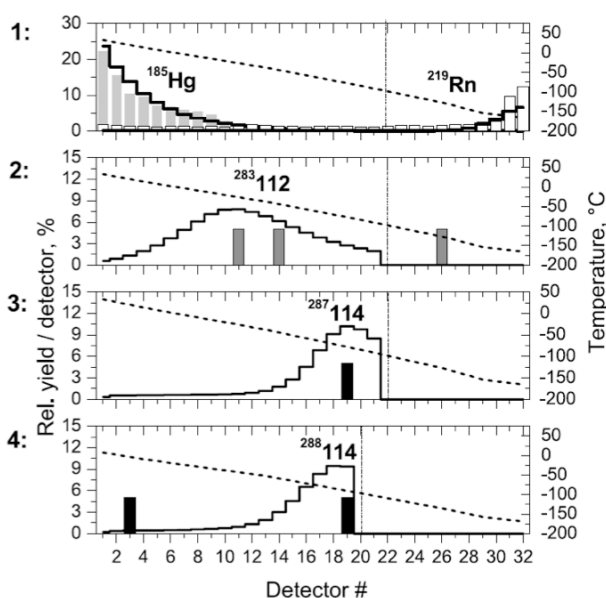


Figure 7. Deposition pattern inside of the detector array for Hg and Rn (top), of three atoms of Cn observed in the ^{242}Pu bombardment (second), of the single atom of element 114 detected in the ^{242}Pu bombardment (third), and of the two atoms of element 114 found in the ^{244}Pu bombardment (fourth) (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.

4. 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}Ca induced fusion reactions with actinides targets. This situation stimulated,

in a first round, chemical studies of Cn and element 114. All information gained so far point to a highly volatile behaviour of both elements.

The actual limit for chemical investigation is limited to isotopes with half-lives of approx. 0.5 s or longer. Future chemical investigation will largely benefit from the “pre-cleaning” strategy developed at Lawrence Berkeley Laboratory [21] and now applied at several other heavy ion labs via placing a physical separator (usually a gas-filled magnet) between the target and a chemical device. This novel approach has not been discussed in this manuscript. The lower production rates (due to thinner targets that can be used) is largely overcompensated by the significantly improved reduction of background signals in the detector arrays.

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