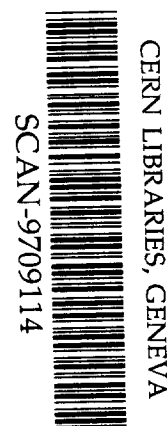PAUL SCHERRER INSTITUT

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Chemistry Gains a New Element: Z = 106

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Abstract: The correct position of a new element in the periodic table is not a trivial matter since relativistic effects can make heaviest elements to behave different from expectations. For the first time, chemical separations of element 106 (Seaborgium[§], Sg) were performed in the gas phase and in aqueous solution followed by an unambiguous identification of this element and/or its α-decay products. Seaborgium was produced at the UNILAC accelerator of the Gesellschaft für Schwerionenforschung in Darmstadt, Germany, in the complete fusion reaction between ^{22}Ne and ^{248}Cm. On the basis of 18 detected atoms of the isotopes ^{265}Sg and ^{266}Sg, which have half-lives of about 7 and 21 s, respectively, it was possible to show that seaborgium is an ordinary member of the periodic table, i.e. it behaves similar to tungsten and molybdenum.

1.Introduction

Calculations of the electron configuration of heaviest elements [1-5] have predicted that sudden changes in the structure of the electron shells may appear due to relativistic effects. Such effects lead to attraction of spherical s and $p_{1/2}$ shells and to expansion of high-angular momentum shells such as d and f orbitals. As a consequence, unexpected chemical properties may result [6-8].

Studies of chemical properties of elements 104 (rutherfordium, Rf) and 105 (dubnium, Db) have been carried out in recent years by several groups [9]. Some of the results were very surprising. E.g. in aqueous phase studies it was found that dubnium behaves more similar to niobium and/or protactinium and not like tantalum [10-12]. In gas phase investigations the observed volatility of rutherfordium chloride was higher than that of hafnium chloride [13,14], opposite to expectations on the basis of estimated trends within group 4 chlorides [15]. In contrast. dubnium bromide (or oxybromide) was found to have a surprisingly low volatility [16].

These findings motivated research in chemical properties of still heavier elements. Of main interest is the question whether the behaviour of seaborgium resembles that of its homologs in the periodic table, tungsten and molybdenum, and possibly also of its pseudo-homolog uranium (Fig. 1).

Such chemical studies could only be envisaged because of the recent discovery of relatively long-lived neutron-rich isotopes of seaborgium [17]. Due to a predicted new magic neutron shell at N = 162 it was found that ^{265}Sg and ^{266}Sg, produced in the reaction ^{22}Ne + ^{248}Cm in 4n and 5n evaporation channels, have surprisingly long half-lives of 2 - 30 s and 10 - 30 s, respectively. The previously known heaviest isotope of seaborgium was ^{263}Sg with a half-life of 900 ms [18,19]. An attempt to perfom a thermochromatographic separation of seaborgium with this short-lived isotope was interpreted by the authors as evidence for the formation of volatile oxychlorides of seaborgium, similar to tungsten [20]. However, the used experimental technique fell short of unambiguously

showing that the observed, by itself unspecific spontaneous-fission decay originated from an isotope of seaborgium.

2. Experimental

Two series of bombardments have been carried out at the UNILAC accelerator of the Gesellschaft für Schwerionenforschung in Darmstadt. In the first series of studies, performed in 1995, a 0.95 mg/cm^2 thick ^{248}Cm target was bombarded by about 2x10^{12} particles/s of 121 MeV ^{22}Ne. From the thin target recoiling products were collected in a thermalization chamber flushed continuously with about 1 l/min of He which contained small (about 0.05 - 0.5 µm) particles of KCl (aqueous phase studies) or graphite (gas phase studies). In a continuous regime, products attached onto the surface of these particles were transported in a few seconds along thin capillaries to the chemistry devices ARCA and OLGA („gas-jet technique"). In a following second experiment, performed in 1996, a mixed ^{248}Cm/^{152}Gd target of 0.69/0.02 mg/cm^2 thickness was bombarded by the same intensity of 123 MeV ^{22}Ne. These experiments were mainly used to further study the gas chemical behaviour of seaborgium. The mixed target allowed a simultaneous production of short-lived isotopes of tungsten and seaborgium. The tungsten isotopes were then used as a tracer to monitor continuously the chemical yield of the separation device.

In the gas phase studies the gas jet was connected to OLGA, the **On-Line Gas chemistry Apparatus** [21] (Fig. 2). Here, the graphite particles were collected on a quartz wool plug positioned in a first part of a quartz chromatography column heated to about 1000 °C. To this position 100 - 140 ml/min of chlorine, saturated with thionyl chloride, and 2 ml/min of oxygen was added. Previous extensive model studies with tungsten and molybdenum have shown [22] that under such conditions most likely the dioxydichloride molecule is formed, i.e. MO_2Cl_2 (M = Mo, W). After

leaving the reaction oven, the volatile molecules had to pass a 1.8 m long 1.0 mm diameter quartz column, inserted into a Carlo-Erba© gaschromatograph. Behind the column, the separated molecules were re-attached onto new aerosol particles of CsCl in 1 l/min of argon and then transported through a 2 mm diameter polyethylene capillary to the rotating wheel counting device ROMA. Here the products were deposited on about 40 $\mu g/cm^2$ thick polypropylene foils, mounted along the circumference of a weel. Every 10 seconds, the freshly deposited samples were moved between 300 mm^2 PIPS (Passivated Ion-implanted Planar Silicon) detector pairs mounted in 7 consecutive positions to count particles in an event-by-event-mode. Such a device allows to measure not only α-particle energies and fission fragment energy spectra but also to search for correlated α-decay chains, spontaneous-fission followed after α-decay (chains), partly using the so-called „mother-daughter" mode [18,19].

Under the chemical conditions used, besides group 6 oxychlorides also group 4 and 5 chlorides and/or oxychlorides might have been formed and transported [22], e.g. rutherfordium tetrachloride or dubnium oxychloride [23]. Actinides are not expected to pass the chromatography column.

In the aqueous phase studies the gas jet was led to the Automated Rapid Chemistry Apparatus ARCA [24]. This device is a micro-computer controlled apparatus for fast, repetitive, and reproducible chromatographic separations in a miniaturized and chemically inert high-performance liquid-chromatography system. There, the reaction products attached to KCl particles were collected for 45 s by inertial impaction in the collection position of ARCA and then eluted within 10 s with a 0.1 M $HNO_3/5x10^{-4}$ M HF solution through a 8x1.5 mm chromatographic column filled with cation exchange resin Aminex [25]. Under such conditions the negative complexes MO_4^{2-}, MO_3F^- or $MO_2F_3^-$, typical for hexavalent ions from group 6 as well as neutral species like MO_2F_2 pass through the column. All positive ions are retained. Within about 28 s after elution final

samples were prepared on Ta discs and then assayed for α-decay and spontaneous-fission in a 2π geometry for 6 min.

3. Results and discussion

3.1 Gas phase chemical studies

Table 1 summarizes all observed decay chains [26]. The SgO_2Cl_2 yields were determined at the four isothermal temperatures 250, 300, 350 and 400 °C, where 0, 4, 8 and 3 atoms, respectively, of ^{265}Sg plus ^{266}Sg were detected. Also listed in table 1 are the the calculated random rates N_R for the different group of events. DM means that these events were observed in the mother-daughter mode, where - after the mother event has been detected - the catcher wheel of the ROMA system was moved in an „off" position with no sample in front of any detector. This mode allows detection of the daughter decay at low background count-rates. As can be read from table 1, out of the detected 15 events 2.9 are expected to be random. For a detailed description of the mathematical procedure to calculate the random rates we refer to [26]. An analysis of the data listed in table 1 results in the following decay properties [26]:

^{265}Sg: $T_{1/2} = 7.4^{+3.3}_{-2.7}$ s (68 % c.i.); E_α : 8.67 - 8.96 MeV

^{266}Sg: $T_{1/2} = 21^{+25}_{-7}$ s (68 % c.i.) ; $E_\alpha = 8.68 \pm 0.14$ MeV;

   spontaneous-fission branch ≤ 80 % (68 % c.i.)

From the number of detected atoms deduced cross sections at a bombarding energy of 121 MeV amount to about 440 and 60 pb for the reactions $^{248}Cm(^{22}Ne,5n)^{265}Sg$ and $^{248}Cm(^{22}Ne,4n)^{266}Sg$, respectively. These values are rough estimates since several yields (e.g. gas-jet transportation, chemical yield) have not been measured.

Figure 3 depicts the chromatographic yield curves for ^{168}W, presumably in form of WO_2Cl_2, and ^{265}Sg + ^{266}Sg, as SgO_2Cl_2, as a function of the isothermal temperature of OLGA . The yield curve for tungsten was measured during the second seaborgium experiment where the target also contained ^{152}Gd. In figure 3 the measured yields for ^{265}Sg and ^{266}Sg at the temperatures 300, 350 and 400 °C were averaged, after being normalized to the applied beam integrals, which were different for the different temperatures [27].

On the basis of a Monte Carlo model [28] from such chromatographic curves adsorption enthalpies ΔH_a^0 of the volatile molecules on the surface of the quartz chromatography column may be deduced. The resulting value is $\Delta H_a^0 = -96$ kJ/mol for WO_2Cl_2, in good agreement with previous studies [22], where 100 - 102 kJ/mol was found for identical chemical conditions. The value for SgO_2Cl_2 is -115 ± 20 kJ/mol. The large error has its origin in the poor statistics as well as in the uncertainties of the ^{265}Sg and ^{266}Sg half-lives. Also shown as shaded area in figure 3 is a theoretical prediction of the chromatographic curve of SgO_2Cl_2 which results from a thermodynamic extrapolation of the adsorption enthalpies of the dioxydichlorides on quartz surfaces within group 6. The resulting theoretical value for ΔH_a^0 is -106 kJ/mol, in good agreement with the experimental result.

As was shown previously [29], adsorption enthalpies of microamounts of a given compound, e.g. chlorides on quartz surfaces, are proportional to the volatility of the corresponding macroamounts. Hence, from this work and ref. [22] the following volatility sequence of the dioxydichlorides of group 6 elements may be derived: $MO_2Cl_2 > WO_2Cl_2 \geq SgO_2Cl_2$. A lower volatility of SgO_2Cl_2 if compared to that of WO_2Cl_2 has also been predicted by a Dirac-Slater discrete-variational calculation [30]. An improved knowledge of the half-lives of ^{265}Sg and ^{266}Sg will in future permit to reduce the experimental error bars of the adsorption enthalpy for SgO_2Cl_2.

3.2 Aqueous phase studies

In the samples prepared from about 3'900 separations 3 decay chains of the daughter and grand-daughter of ^{265}Sg, ^{261}Rf and ^{257}No, respectively, were observed (Fig. 4). Obviously, due to the time regime (see experimental) the mainly produced ^{265}Sg atoms have been separated by ARCA but have not survived the approximate half-minute time span needed to prepare final samples and start counting. Since under the given conditions rutherfordium does not pass through the Aminex column - as shown in an independant experiment [31] - and also because direct production of ^{261}Rf is very unlikely for nuclear physics reasons (at the used bombarding energy the corresponding α5n-reaction channel is not populated) the observed decay chains can indeed be interpreted as a proof for a separation of seaborgium. An analysis showed that for this group of events 0.56 could be random which is equal to a 0.24 % probability that all 3 events are random [25].

3.3 Summary and outlook

The reaction 121 and 123 MeV ^{22}Ne on ^{248}Cm was used to produce ^{265}Sg and ^{266}Sg. On the basis of 15 atoms of ^{265}Sg + ^{266}Sg it was possible to show that seaborgium forms a volatile oxychloride, presumably SgO_2Cl_2, of lower or equal volatility compared to that of WO_2Cl_2, in full agreement with expectation. Moreover, with only three atoms of ^{265}Sg it was possible to show that in dilute nitric acid/hydrofluoric acid seaborgium elutes through a cation exchange column in form of a negative - or possibly neutral - complex. Also this behaviour is expected for group 6 elements.

As an additional result, for the first time, the half-lives of the two isotopes ^{265}Sg and ^{266}Sg could be determined.

One of the separation techniques, the on-line gas chemistry apparatus OLGA, might be ideally suited for further studies of the elements 107 (bohrium, Bh) and 108 (hassium, Hs). For hassium the presently known longest-lived isotope is ^{269}Hs which has a half-life of about 9 s [32]. For bohrium it seems reasonable to assume that the isotopes ^{266}Bh and ^{267}Bh have half-lives of several seconds. For a gas chemical separation of these two elements the volatile species proposed previously [33] should be envisaged, i.e. the acid $HBhO_4$ and the oxyde HsO_4. The deposition temperatures of these species in a thermochromatography quartz column were estimated as 100 °C and - 80 °C, respectively [33]. For production the reactions ^{249}Bk(^{22}Ne,5n)^{266}Bh - with an estimated cross section of about 10^2 pb - and ^{248}Cm(^{26}Mg,5n)^{269}Hs - with an estimated cross section of a few pb - might be used. The sensitivity of the present-day OLGA technique seems sufficient for a chemical study of bohrium, since it has also been used successfully to investigate ^{266}Sg, produced with only 40 pb cross section. However, for a future study of hassium, a significant improvement is required to increase to overall yield of the technique, which is presently only a few percent. This seems possible if the reaction products are converted to the volatile species *in-situ*, i.e. in the thermalization chamber at the accelerator. Such an approach has been used at Dubna over many years [34]. In case of hassium, the thermalization gas should be oxygen, in order to form the gaseous tetroxyde directly from the stopped atoms (or ions) [35].

Acknowledgements

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Table 1: Correlated decay chains observed in the OLGA experiments with E_α (mother) = 8.57 - 9.07 MeV (^{265}Sg) and E_α (daughter(s)) = 8.05 - 8.45 MeV (^{261}Rf, ^{257}No) or E_α (mother) = 8.41 - 8.85 MeV (^{266}Sg) and E_{sf} (daughter) $\geq$ 20 MeV (^{262}Rf) within 6.3 s. DM indicates event chains observed in the „mother-daughter" mode (see text). N_R is the number of calculated random correlations for the corresponding group of events.

Decay chain	E_1 (MeV)	t_1 (s)	E_2 (MeV)	Δt_2 (s)	E_3 (MeV)	Δt_3 (s)	Mode	Decay assignment	Isothermal Temperature	N_R
1	8.86	0.6	8.35	48.4	-	-	DM	^{265}Sg $\to$ ^{261}Rf or ^{257}No	300 °C	
2	8.76	1.4	8.39	151.8	-	-	DM	^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	
3	8.93	7.0	8.22	22.2	-	-	DM	^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	0.83
4	8.82	27.3	8.15	53.3	-	-	DM	^{265}Sg $\to$ ^{261}Rf or ^{257}No	300 °C	
5	8.81	2.8	8.36	31.0	8.11	14.8		^{265}Sg $\to$ ^{261}Rf$\to$^{257}No	400 °C	0.04
6	8.69	1.4	8.18	56.0	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	300 °C	
7	8.85	5.6	8.41	40.2	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	
8	8.76	6.6	8.28	45.8	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	
9	8.77	6.8	8.22	25.5	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	1.90
10	8.96	12.8	8.23	23.5	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	
11	8.85	19.1	8.35	0.5	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	400 °C	
12	8.93	19.1	8.41	35.6	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	350 °C	
13	8.86	21.7	8.37	31.6	-	-		^{265}Sg $\to$ ^{261}Rf or ^{257}No	300 °C	
14	8.79	15.1	SF	1.7	-	-		^{266}Sg $\to$ ^{262}Rf	350°C	0.09
15	8.52	48.9	SF	2.8	-	-	DM	^{266}Sg $\to$ ^{262}Rf	400°C	0.03

Figure captions

Fig. 1: Periodic table of the elements. For the transactinides the names proposed by a IUPAC commission in 1997 are used. The elements Sg through 112 are plotted as a group outside of the periodic table to indicate that no chemical information on them is available yet.

Fig. 2: The OLGA system used for the study of seaborgium. The gas-jet transports the seaborgium atoms attached to carbon particles in a helium gas to the reaction oven, where the reactive gas $Cl_2/SOCl_2/O_2$ is added to form volatile oxychlorides and to convert the carbon particles into CO_2. Behind the isothermal chromatography section the ejecting molecules are attached to new particles and then transported to the counting device ROMA.

Fig. 3: Measured relative yield of ^{168}W (presumably in form of WO_2Cl_2) in the ROMA device as a function of the isothermal part of OLGA (closed squares). Also shown are the simultaneously measured yields of ^{265}Sg + ^{266}Sg (see table 1) (open triangles). To reduce error bars, the experimental yields at 300, 350 and 400 °C were averaged to one value. The ordinate on the right side gives the number of detected seaborgium atoms per 10^{17} ^{22}Ne particles applied to the experiment. This corresponds to roughly 7 hours of beam time per detected atom. The dashed lines represent the expected behaviour of seaborgium (see text).

Fig. 4: Observed decay chains in the ARCA experiment for a total beam integral of 5.5×10^{17} ^{22}Ne particles applied to the target.
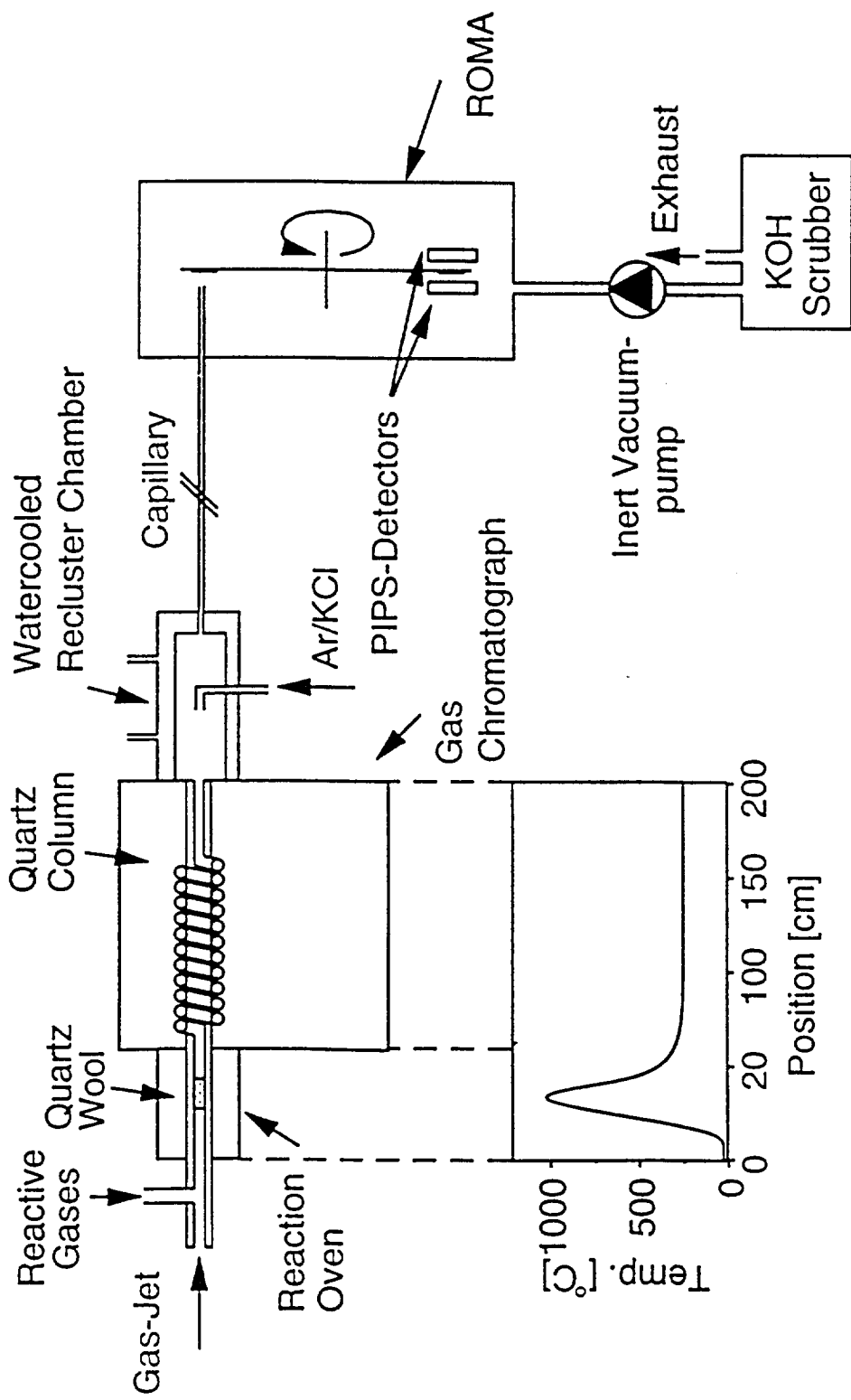
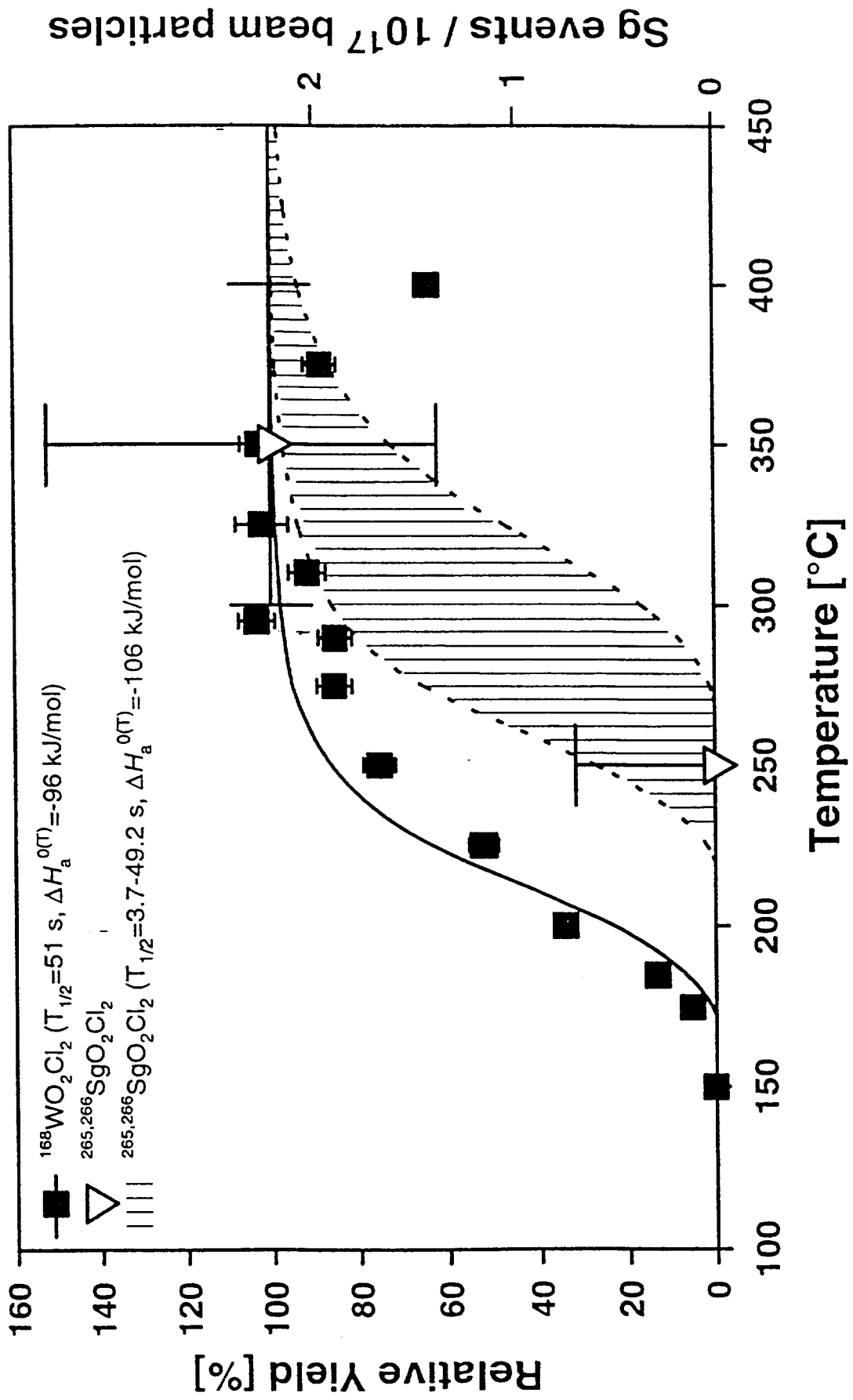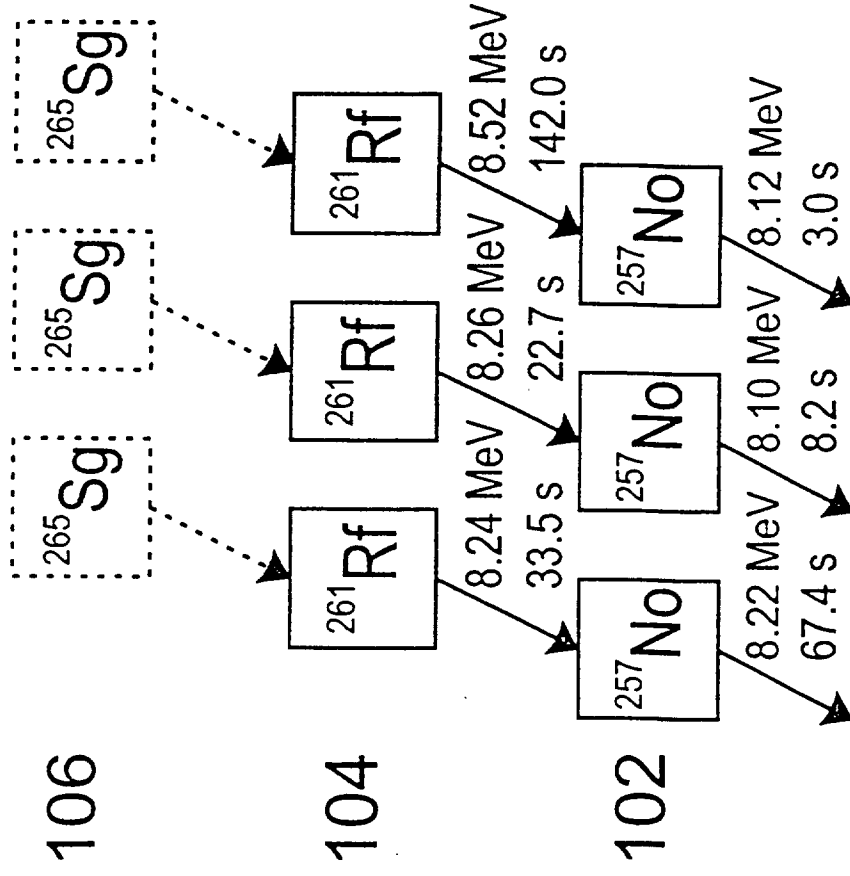| 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac+	Rf	Db	**Sg** ←	Bh	Hs	Mt	110	111	112						

+actinides

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

*lanthanides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Fig. 1

Fig. 2

Fig. 3

Fig. 4