After the Actinides, then what?

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1 Introduction and Historical Perspective

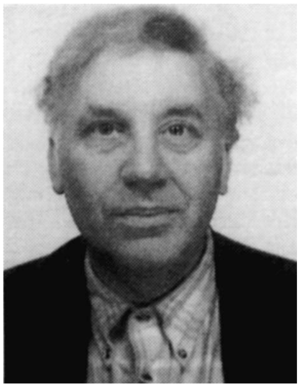
Mendeleev's creation of the Periodic Table depended on the discovery of a considerable number of chemical elements in the preceding century. A key element in his scheme was its basis on patterns and trends in physical and chemical properties (and not, as chemists unconsciously (but frequently) seem to assume, quantum mechanics). This meant that he was able to recognise that iodine belonged in Group VII with the halogens, rather than with the chalcogenides in Group VI; further, he left gaps for as yet undiscovered elements, such as eka-boron (Sc), eka-silicon (Ge) and eka-aluminium (Ga), for which he was able to propose properties, based upon interpolation between those of the known elements. Subsequent modification accommodated the lanthanides (and of course the noble gases) and although up until the Second World War the elements Ac–U were placed in Groups IIIA–VIA (3—6), Seaborg developed an actinide concept parallel to the lanthanide series in which the 5f orbitals are filled. Up to then, thorium was generally thought to be a heavier version of hafnium in Group IVA (4) and uranium a heavier homologue of tungsten in Group VIA (6), though Werner had proposed an essentially modern long form of the Periodic Table in which the transradium elements were classed with the lanthanides,[1] whilst other classifications of this type were made[2] in the 1920s and 1930s. The later discovery that the heavier actinides, synthesized in the 1940s and 1950s, exhibited lanthanide-like behaviour, prompted Seaborg's hypothesis. It may be remarked that the usual arrangement of the Periodic Table takes the lanthanides to run from Ce to Lu and the actinides from Th to Lr, but an alternative view[3] takes the lanthanides from La to Yb and the actinides from Ac to No. This would make lawrencium the first member of the fourth transition series and the first transactinide.

After the discovery of lutetium in 1907, the lanthanide series was complete, save for the synthesis of radioactive promethium at the end of the Second World War. The other gaps in the Periodic Table were filled with the discovery of hafnium and rhenium, together with the synthesis of technetium. Extension became possible with the synthesis of the elements after uranium [uranium is the heaviest element that is found in the earth with a comparable lifetime in macroscopic amounts, though long-lived ^{244}Pu ($t_{\frac{1}{2}} = 8 \times 10^7$ y) also exists in nature in trace amounts, having been detected in a rare earth ore]. By 1961, the last of the actinides, lawrencium (Lr), had been synthesized; the first isotope claimed (257, later found to be 258) was synthesized by bombarding a mixture of californium isotopes (249—252) with ^{10}B and ^{11}B nuclei:

$$^{249}\mathrm{Cf} + {}^{11}\mathrm{B} \rightarrow {}^{258}\mathrm{Lr} + 2\,{}^{1}\mathrm{n}$$

It has a half-life of 4.3 s, though the most stable isotope now known is the more neutron-rich ^{262}Lr with a half-life of 216 minutes. By the time lawrencium was first reported, prospects for synthesizing heavier atoms seemed limited. Whilst half-lives for α-decay for the longest-lived isotope were growing steadily shorter with increasing atomic number, the drop in half-lives for spontaneous fission was even more marked. Extrapolation indicated that elements with atomic numbers in the region of 107—108 would become so short-lived ($t_{\frac{1}{2}} = 10^{-3}$ s) that it would be impossible to isolate further elements (Fig. 1). Shortly afterwards, however, theoretical calculations indicated that nuclei with atomic numbers of around 114 could be unexpectedly stable.[4]

Simon Cotton, a native of Norfolk, graduated from Imperial College, London with BSc and PhD degrees in 1970. Following postdoctoral work on organolanthanides at Queen Mary College, London, where Alan Hart gave him a continuing interest in the f-block elements, he spent a further period of research at the University of East Anglia, where ESR studies on iron compounds did not stop his research into the dates of construction of the later Gothic churches of East Anglia. Since 1977 he has been earning a living as a schoolteacher and his current interests include writing a book on Precious Metal Chemistry and finding a permanent job.



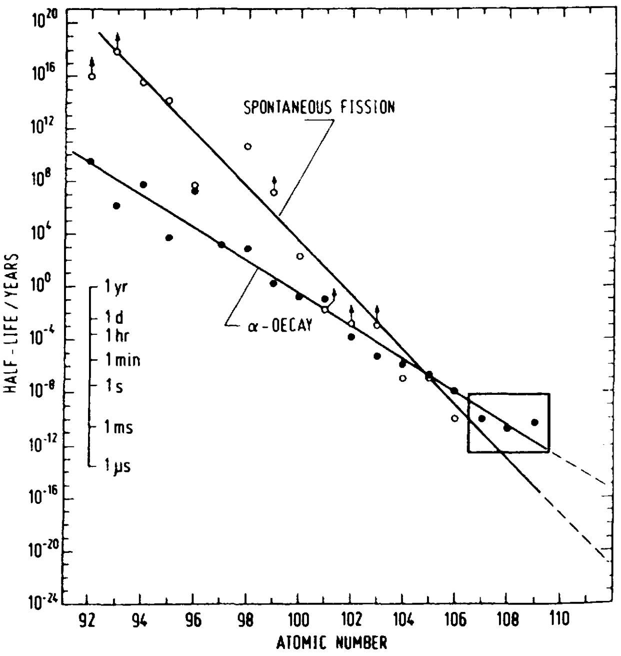


Figure 1 Half-lives for α-decay and spontaneous fission of the actinides and early transactinides.
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The stability of a nucleus (based on a model of nuclear stability analogous to that of the Rutherford–Bohr model of electronic structure) is determined by the inter-nucleon forces; an attractive force between all nucleons and a Coulombic repulsion force between protons, the latter becoming proportionately more important as the number of protons increases. Extra stability is associated with filled shells of nucleons, 'magic numbers;' for neutrons they are 2, 8, 20, 28, 50, 82, 126, 184 and 196 and for protons 2, 8, 20, 28, 50, 82, 114 and 164. Nuclei with closed shells of nucleons are stabilised, particularly against spontaneous fission. Nuclei where both the numbers of protons and neutrons are magic numbers ('double-magic' nuclei) are particularly stable, such as ^{4}He, ^{16}O, ^{40}Ca and ^{208}Pb. After ^{208}Pb, the next 'double-magic' nucleus would be ^{298}114. Three-dimensional maps were drawn[5] to

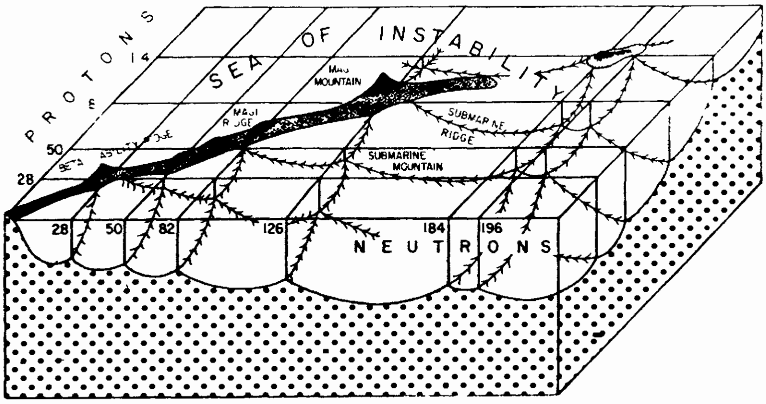

Figure 2 Known and predicted regions of nuclear stability (Reproduced with permission from *J Chem Educ* , 1969, **46**, 631)

express the stability of these nuclei (Fig 2), the stability of the isotope is represented by the height of the peak, so that 'magic number' nuclei correspond to peaks The original picture, which showed a 'sea of instability' between the later actinides and element 114, has been supplanted by subsequent calculations indicating that there may be relatively stable nuclei extending out to the 'island' with atomic number 114

2 Looking for transactinide elements in nature[6—8]

Once theoreticians had predicted that elements with $Z = ca$ 110—126 might be stable, scientists attempted to synthesize them, and also to see whether they had led a hitherto undiscovered existence in nature Predicted half-lives of $^{294}[110]$[†] (an atom with a magic number of 184 neutrons) vary from 0 1 million to 2 5 billion years, a half-life of 2×10^8 years would be long enough for survival of such atoms from the formation of the earth's crust 4×10^9 years ago Searches for element 110 (eka-platinum) in platinum metal ores led to negative results, corresponding to a limit of 10^{-11} g per g stable element Similar inconclusive results were obtained looking for element 114 (eka-lead) in lead ores Other experiments examined extra-terrestrial samples, *e g* meteorites, similarly, it had been thought that rapid neutron capture in supernovae by heavy nuclei would create superheavy elements, but this is not now thought to be the case In some of these experiments, detection limits were as low as 10^{-16} g per g

3 Synthesis of Transactinides

The methods used to synthesize the elements from element 104 onwards have needed to be more sophisticated than those first used for transuranium elements The elements following uranium were first synthesized by neutron irradiation of earlier elements like uranium as with the synthesis of neptunium and plutonium

$$^{238}U + {}^{1}n \rightarrow {}^{239}U$$

$$^{239}U \rightarrow {}^{239}Np + \beta$$

$$^{239}Np \rightarrow {}^{239}Pu + \beta$$

Here the initial product is a heavier isotope of the target atom (uranium) which increases in atomic number on subsequent β-decay This route has the disadvantage that each new nucleus is just one mass unit heavier than its predecessor but it did permit high-yield synthesis in nuclear reactors where an intense neutron flux was possible and far more spectacularly in the first syntheses and identifications of einsteinium and fermium (elements 99 and 100) in the debris of atom bomb explosions at Eniwetok atoll in 1952 The heaviest nucleus that can be synthesized in this way is ^{257}Fm as many of the nuclei beyond this have such short half-lives that their further irradiation is impossible (thus ^{258}Fm whose $t_{½}$ is 0 4 ms undergoes almost instantaneous decay by spontaneous fission)

For heavier nuclei than $Z = 100$, the approach used is to bombard a target nucleus (generally an actinide) with the positively charged nuclei of other elements, using a particle accelerator (cyclotron or linear accelerator) to supply the high energy needed to overcome the repulsion between the positively charged target nucleus and positive projectile nucleus This synthetic route essentially adds all the additional mass needed for the desired product in one stage (though sometimes neutrons are lost)

$$^{246}Cm + {}^{12}C \rightarrow {}^{254}No + 4{}^{1}n$$

A disadvantage of this method is that the atoms are produced one at a time, obviating 'normal' chemical experiments on bulk samples The chance of a collision producing a combined nucleus is in the order of one in a billion (10^9) collisions at best A further risk is the possibility of the nucleus produced by fusion of the projectile and the target undergoing fission, because it is in an excited nuclear state It can get rid of its excess energy in two ways one is the emission of neutrons and γ-rays, the other route being fission (Fig 3) (If the energy of the bombarding particles is too low, they do not possess enough energy to overcome the Coulombic repulsion between them)

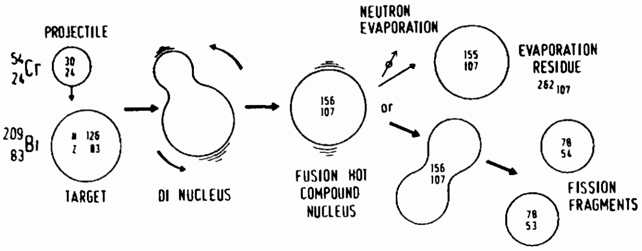

Figure 3 Synthesis of element 107 by nuclear fusion (Reproduced with permission from *Angew Chem Int Ed Engl* , 1988, **27**, 1421)

An essential part of the syntheses of the elements from $Z = 107$ onwards indeed is to use the minimum kinetic energy of the bombarding particle *just* to result in fusion (sometimes known as a cold fusion approach, despite the resulting confusion in name), this means that the product nucleus has little excess energy to get rid of, so that not only is the likelihood of fission minimized, but very few neutrons 'evaporate' from the 'hot' nucleus, so that the mass number of the resulting product is as high as possible This is important, as neutron-rich isotopes are likely to be more stable

4 Syntheses of the Elements

These have been carried out by three research groups 1, The Lawrence Berkeley Laboratory, University of California, Berkeley, USA, 2, Joint Institute for Nuclear Research, Dubna, USSR, 3,

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[†] Throughout this review atomic numbers enclosed in square brackets are used to represent the transactinides

Laboratory for Heavy Ion Research, Darmstadt, Germany The discovery of elements 104—106 in particular has been claimed by two groups, it is difficult to assign priority in discovery (and the resulting traditional right to name the elements) because of the incredibly small quantities of the elements reported and because different groups have reported different isotopes which decay in different ways and were detected by different methods [9] The Transfermium Working Group of the International Union of Pure and Applied Chemistry in conjunction with the International Union of Pure and Applied Physics was set up in 1985 to consider priority of discovery of these elements and made its recommendations in 1992 [10] These proved controversial, provoking responses from all the centres involved [11] In this article a neutral standpoint has been adopted, the elements being referred to by their atomic numbers rather than one of the suggested symbols

Element 104 was first claimed by Russian workers in 1964 In 1969 workers from Berkeley reported the synthesis of $^{257-259}[104]$

$$^{249}\mathrm{Cf} + {}^{12}\mathrm{C} \rightarrow {}^{257}[104] + 4\,{}^{1}\mathrm{n}$$

$$^{249}\mathrm{Cf} + {}^{13}\mathrm{C} \rightarrow {}^{259}[104] + 3\,{}^{1}\mathrm{n}$$

$$^{248}\mathrm{Cm} + {}^{16}\mathrm{O} \rightarrow {}^{258}[104] + 6\,{}^{1}\mathrm{n}$$

Almost simultaneously an alternative route was reported by the Dubna workers

$$^{242}\mathrm{Pu} + {}^{22}\mathrm{Ne} \rightarrow {}^{260}[104] + 4\,{}^{1}\mathrm{n}$$

$$^{242}\mathrm{Pu} + {}^{22}\mathrm{Ne} \rightarrow {}^{259}[104] + 3\,{}^{1}\mathrm{n}$$

Element 105 was reported by the Berkeley group in 1970 and the Dubna group in 1971 The Berkeley team used

$$^{249}\mathrm{Cf} + {}^{15}\mathrm{N} \rightarrow {}^{260}[105] + 4\,{}^{1}\mathrm{n}$$

whilst the Dubna group employed

$$^{243}\mathrm{Am} + {}^{22}\mathrm{Ne} \rightarrow {}^{260}[105] + 5\,{}^{1}\mathrm{n}$$

Element 106 was reported by the Berkeley group in 1974 and the synthesis repeated there by a different team in 1993

$$^{249}\mathrm{Cf} + {}^{18}\mathrm{O} \rightarrow {}^{263}[106] + 4\,{}^{1}\mathrm{n}$$

Atoms with or near a deformed neutron shell at $N = 162$ and $P = 108$ are thought to be relatively stable to spontaneous fission,[12] a view supported by the isolation of $^{265}[106]$ and $^{266}[106]$ with estimated half-lives of 2—30 s and 10—30 s

$$^{248}\mathrm{Cm} + {}^{22}\mathrm{Ne} \rightarrow {}^{265}[106] + 5\,{}^{1}\mathrm{n}$$

$$^{248}\mathrm{Cm} + {}^{22}\mathrm{Ne} \rightarrow {}^{266}[106] + 4\,{}^{1}\mathrm{n}$$

The Darmstadt group used rather heavier projectile atoms and a concomitantly lighter target in their approach to elements 107—111 (Russian workers have reported less detailed studies on 107 and 108) As mentioned above, the group uses the minimum energy necessary for fusion to occur Another point to appreciate is that the Pb and Bi targets have magic or near magic-number structures, as do the nickel projectile nuclei used in the syntheses of elements 110 and 111, so that a large part of the projectile energy is consumed in breaking into the filled shell and it therefore reduces the possibility of the new nucleus undergoing fission, an approach first suggested by Oganessian [13]

$$^{209}\mathrm{Bi} + {}^{54}\mathrm{Cr} \rightarrow {}^{262}[107] + {}^{1}\mathrm{n}$$

$$^{208}\mathrm{Pb} + {}^{58}\mathrm{Fe} \rightarrow {}^{265}[108] + {}^{1}\mathrm{n}$$

$$^{209}\mathrm{Bi} + {}^{58}\mathrm{Fe} \rightarrow {}^{265}[109] + {}^{1}\mathrm{n}$$

The recent Darmstadt syntheses of elements 110 and 111 have led to the formation of new isotopes $^{268}[109]$ (70 ms) and $^{264}[107]$ (440 ms) Attempts at synthesis of a more stable neutron-rich $^{270}[107]$ have not met with success [14] Theoreticians have predicted the enhanced stability for atoms with around 108 protons and 162 neutrons is due to an effect of their distorted neutron and proton subshells [15] $^{270}[108]$ has a predicted half-life against spontaneous fission of some 30 y, but has so far defied synthesis

In 1994, the GSI group reported[16 17] the syntheses of elements 110 and 111 Bombardment of ^{208}Pb with ^{62}Ni was reported to lead to $^{269}[110]$, which has a half-life of some 393 microseconds and ^{208}Pb with ^{64}Ni was reported to lead to $^{271}[110]$, which has a half-life of 1 5 milliseconds, similarly, bombardment of ^{209}Bi with ^{64}Ni led to $^{272}[111]$, with a half-life *ca* 1 5 milliseconds

$$^{208}\mathrm{Pb} + {}^{62}\mathrm{Ni} \rightarrow {}^{269}[110] + {}^{1}\mathrm{n}$$

$$^{208}\mathrm{Pb} + {}^{64}\mathrm{Ni} \rightarrow {}^{271}[110] + {}^{1}\mathrm{n}$$

$$^{209}\mathrm{Bi} + {}^{64}\mathrm{Ni} \rightarrow {}^{272}[111] + {}^{1}\mathrm{n}$$

An experiment carried out in 1991 and reported in 1995 by the Berkeley group is claimed[18] to have made one atom of the α-emitter $^{267}[110]$ thus

$$^{209}\mathrm{Bi} + {}^{59}\mathrm{Co} \rightarrow {}^{267}[110] + {}^{1}\mathrm{n}$$

whilst a 1994 Dubna–Livermore collaboration[19] has given $^{273}[110]$

$$^{244}\mathrm{Pu} + {}^{34}\mathrm{S} \rightarrow {}^{273}[110] + 5\,{}^{1}\mathrm{n}$$

Table 1 Half-lives and decay modes for the isotopes of elements 104–111

Element	Half life	Decay mode	Element	Half life	Decay mode
104			**107**		
253	1 5 s	SF, α	261	12 ms	α, SF?
254?	0 5 ms	SF	262	8 ms/0 1 s	α,α
255	1 4 s	SF, α?	264	440 ms	α
256	7 ms	α, SF			
257	4 8 s	α, SF	**108**		
258	13 ms	SF, α?	264	0 08 ms	α, SF?
259	3 0 s	α, SF	265	2 ms	α
260	20 ms	SF			
261	65 s	α, SF?	**109**		
262	47 ms	SF?	266	3 4 ms	α
			268	70 ms	α
105					
255	1 5 s	SF, α?	**110**		
257	1 3 s	α, SF	267	4 μs	α
258	4 4 s	EC, α	269	0 17 ms	α
260	1 5 s	α, SF	271	1 1 ms	α
261	1 8 s	α, SF			
262	34 s	EC, α	**111**		
263	27 s	SF, α	272	1 5 ms	α
106					
259	0 5 s	α, SF			
260	4 ms	α, SF			
261	0 3 s	α, SF?			
263	0 9 s	α, SF			
265	2—30 s	α			
266	10—30 s	α			

5 Other Attempts to make Superheavy Elements

A number of unsuccessful attempts have been made, including

$$^{40}\mathrm{Ar} + {}^{248}\mathrm{Cm} \rightarrow x\,{}^{1}\mathrm{n} + {}^{288-x}[114]$$

$$^{48}\mathrm{Ca} + {}^{248}\mathrm{Cm} \rightarrow {}^{1}\mathrm{n} + {}^{295}[116]$$

$$^{76}\mathrm{Ge} + {}^{232}\mathrm{Th} \rightarrow x\,{}^{1}\mathrm{n} + {}^{308-x}[122]$$

$$^{238}\mathrm{U} + {}^{238}\mathrm{U} \rightarrow {}^{298}[114] + {}^{178}\mathrm{Yb}$$

Other suggestions have included bombarding tungsten with ^{140}Ce as a possible route to $^{324}[116]$ Much may depend on the use of neutron-rich projectiles like ^{70}Zn and ^{76}Ge in the synthesis of elements 112—114

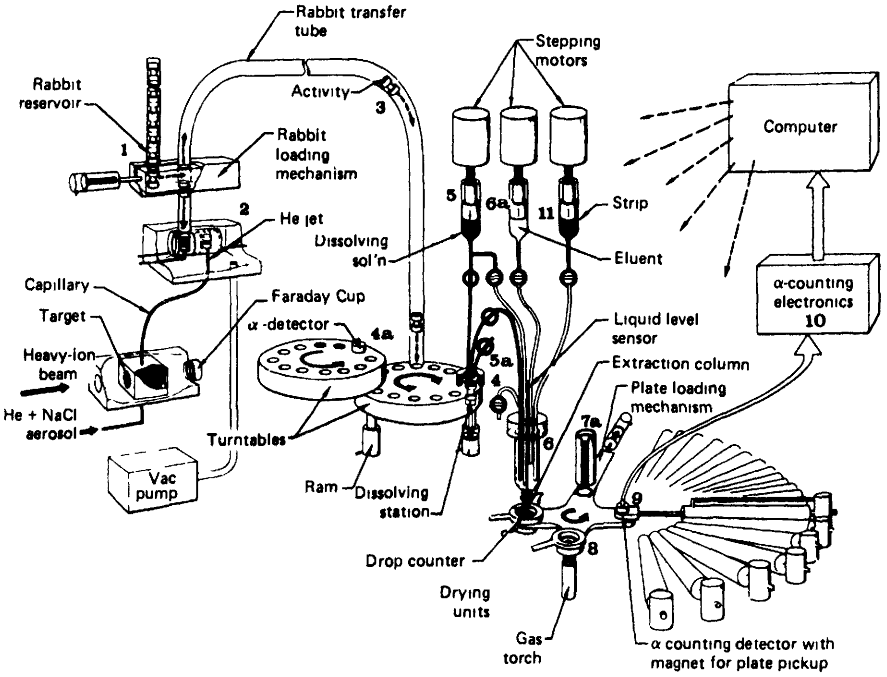

Figure 4 Computer-controlled apparatus for the study of element 104 (Reproduced with permission from *J Inorg Nucl Chem* . 1980, **42**, 80)

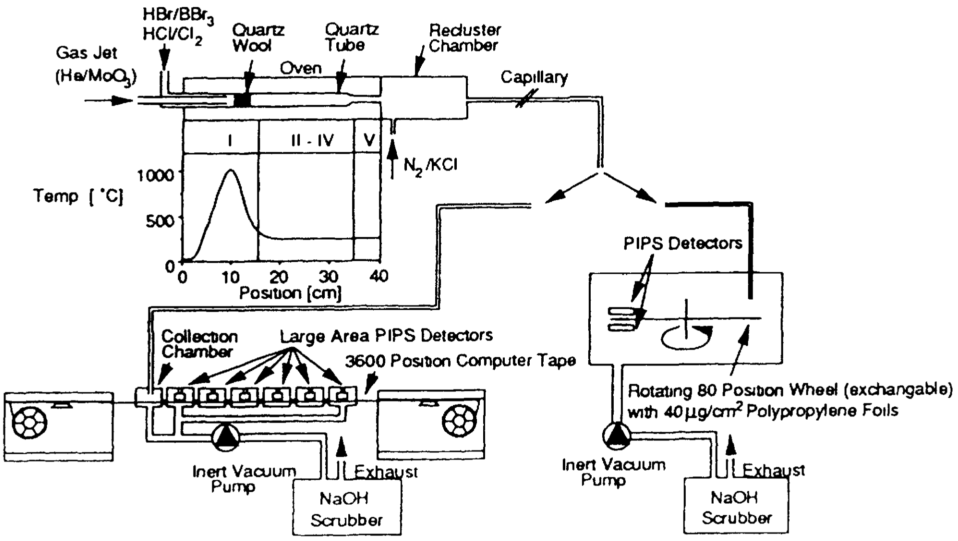

Figure 5 Apparatus for the study of the volatile halides of elements 104 and 105 (Reproduced with permission from *J Alloys Compd* . 1994, **213/214**, 22)

6 Identifying the Elements

Some techniques needed to carry out chemical studies on these elements were first developed during the study of the later actinides, where classical chemical routes became impractical with ultrasmall quantities of very radioactive, short-lived atoms The even shorter half-lives of the elements after 103 meant that they had to be rapidly removed from the accelerator target for chemical study This was achieved by the recoil of the new atom from the target and its transport by a potassium chloride or sodium chloride aerosol in a current of helium to a collection site Fig 4 shows the relatively early system used[20] to study element 104, the sample was deposited on the bottom of a polypropylene 'rabbit' which was then transported to a turn-table, from where it could be α-counted or dissolved, chromatographed, evaporated and α-counted, all within a relatively small period of time (3 minutes in this example)

Recent experiments[21] used a MoO_3 aerosol to transport the atoms prior to halogenation (Fig 5) The volatile halides formed were transported by the helium along the latter part of the tube, which acts as an isothermal gas chromatography column, on leaving the quartz tube they were attached to new aerosols and detected either with a rotating wheel system or on a moving computer tape

In the case of elements 107—111, the millisecond half-lives (Table 1) are too short for there to be any chance of carrying out chemical separations, physical separations and accompanying detection methods are appropriate The Darmstadt group have used[4] a 'velocity filter' which relies on electric and magnetic fields to separate the excess of fast-moving 'projectile' nuclei from slow-moving products recoiling from the target so that the reaction products can be detected (Fig 6) Magnetic lenses are used to focus the beams which are then separated by electric and magnetic fields before colliding with solid-state detectors

Detection of these elements relies on studying their radioactive decay, which is usually either α-emission or spontaneous fission A time-correlation process is used, in this, a solid state detector monitors both the time and position of arrival of fusion products Subsequent decay events *at this position* give not just the decay information of the atom (half-life, α particle energy) but also the corresponding information for its decay products, which are recognizable and thus 'known' nuclei This therefore gives a history

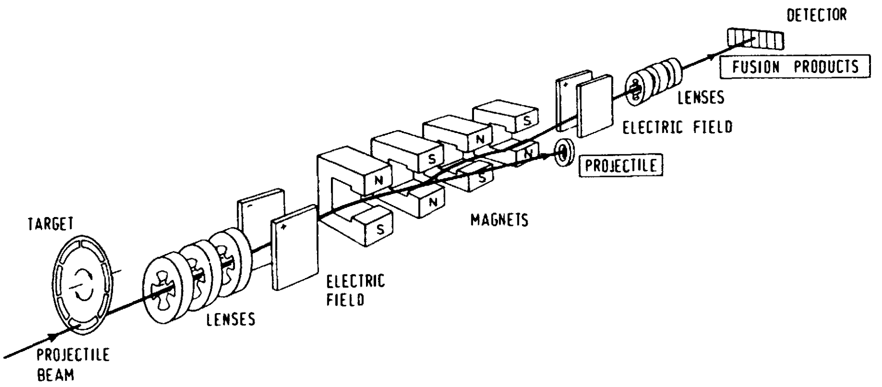

Figure 6 Velocity filter SHIP to separate transactinide fusion products from the projectile beam (Reproduced with permission from *Angew Chem Int Ed Engl*, 1988, **27**, 1422)

of stepwise decay of the initial product Thus in the synthesis of $^{262}[105]$ decay events were observed for the known ^{258}Lr ($t_{1/2}$ = 4 3 s) and its parent, $^{262}[105]$ ($t_{1/2}$ = 34 s) Similarly, reaction of ^{209}Bi with ^{54}Cr led to very short-lived nuclei ($t_{1/2}$ = 4 7 ms) emitting α particles with an energy of 10 38 MeV This α-emitter correlated with a decay chain composed of three successive α-emitters, identified as $^{258}[105]$ (4 4 s, α-particles of 9 17 MeV), ^{254}Lr (13 s, α-particles of 8 46 MeV), and ^{250}Md (52 s, α-particles of 7 75 MeV) The product of the fusion reaction was thus $^{262}[107]$

$$^{209}\mathrm{Bi} + {}^{54}\mathrm{Cr} \rightarrow [107] + {}^{1}\mathrm{n}$$

$$^{262}[107] \rightarrow {}^{258}[105] + {}^{4}\mathrm{He}$$

$$^{258}[105] \rightarrow {}^{254}\mathrm{Lr} + {}^{4}\mathrm{He}$$

$$^{254}\mathrm{Lr} \rightarrow {}^{250}\mathrm{Md} + {}^{4}\mathrm{He}$$

For elements 108—111 the chains are

$$^{265}[108] \rightarrow {}^{261}[106] \rightarrow {}^{257}[104] \rightarrow {}^{253}\mathrm{No}$$

$$^{266}[109] \rightarrow {}^{262}[107] \rightarrow {}^{258}[105]$$

$$^{269}[110] \rightarrow {}^{265}[108] \rightarrow {}^{261}[106] \rightarrow {}^{257}[104]$$

$$^{272}[111] \rightarrow {}^{268}[109] \rightarrow {}^{264}[107] \rightarrow {}^{260}[105] \rightarrow {}^{256}[103]$$

The limiting factor in detecting the reaction product is thus the time of flight of the product from the target to the detector, which is of the order of microseconds

7 Naming the Elements

Who has the right to name an element, the first person to make it or the first person explicitly to identify it? The two groups who claim to have synthesized elements 104 and 105 gave them both a name The International Union of Pure and Applied Chemistry therefore suggested a system of surrogate names for these elements until definite identification could be credited, this assigned each element a name based on its atomic number, using the 'code' 0 = nil, 1 = un, 2 = bi, 3 = tri, 4 = quad, 5 = pent, 6 = hex, 7 = sept, 8 = oct and 9 = en Thus element 104 is unnilquadium

The synthesizers for element 104 suggested names commemorating Ernest Rutherford and Igor Kurchatov, the Soviet nuclear physicist The American suggestion for 105 honoured German physicist Otto Hahn whilst the Russian alternative was in honour of the Danish originator of atomic theory, Niels Bohr Recent confirmation of the synthesis of element 106, first synthesized in 1974, permitted the suggestion of the name seaborgium after Glenn Seaborg, discoverer of many of the radioactive elements over the past 50 years The German synthesizers of elements 107—109 gave them names in 1992 commemorating respectively Niels Bohr, the State of Hesse where element 108 was first synthesized (like californium), and Lise Meitner, the Austrian nuclear physicist and researcher into nuclear fission The American Chemical Society's Nomenclature Committee have accepted the German suggestions for 107—109 (general acceptance of the proposal for 107 would remove the dichotomy for element 105) The recent IUPAC proposals, still to be ratified by its Council, call element 104 dubnium, after the Russian laboratory, whilst the name joliotium for element 105 honours the French nuclear scientist Jean-Frédéric Joliot-Curie and 106 becomes rutherfordium Elements 107 through 109 become bohrium, hahnium and meitnerium respectively (Table 2) These proposals have proved highly controversial, a reason given for not adopting the American suggestion of seaborgium for element 106 is that it was felt that elements should not be named after a living person as naming requires the 'perspective of history ' It is probable that American texts will continue to refer to element 106 as seaborgium, whilst the German group has expressed disquiet at not being able to exercise their prerogative of naming the elements The reported IUPAC comment that the German proposal for naming element 108 after the state in which it was discovered was obscure ignores the precedents of elements like ytterbium and californium and moreover sits oddly with IUPAC's suggestion for element 104

Table 2 Proposed names and symbols for elements 104—109

At No	Name	Symbol	ACS Proposal
101	Mendelevium	Md	Mendelevium
102	Nobelium	No	Nobelium
103	Lawrencium	Lr	Lawrencium
104	Dubnium	Db	Rutherfordium
105	Joliotium	Jl	Hahnium
106	Rutherfordium	Rf	Seaborgium
107	Bohrium	Bh	Nielsbohrium
108	Hahnium	Hn	Hassium
109	Meitnerium	Mt	Meitnerium

8 The Chemistry of Elements 104 and 105

These relatively long-lived elements are the only trans-actinides for which 'real' chemical experiments have been carried out, so far this relates to aqua ions and halides

8.1 Element 104[22–26]

The aqua ion of element 104 is eluted as the α-hydroxybutyrate complex from cation exchange resins much earlier than trivalent actinides, because it is more weakly absorbed by the resin, its behaviour resembling Zr and Hf This supports the assignment of a +4 oxidation state It is extracted from concentrated HCl as anionic chloro complexes, unlike trivalent actinides and Group I and II metals, these complexes are eluted from anion exchange resins with zirconium and hafnium but later than actinides At high chloride concentrations it is extracted into tributyl phosphate more weakly than Zr, Hf and Th but rather like Pu^{IV}, possibly as a complex $[104]Cl_6^{2}$ Like Zr and Hf, however, it forms stable anionic fluoro complexes adsorbed on an anion exchanger The volatility of $[104]Cl_4$ (condensing *ca* 220 °C) is similar to that of $ZrCl_4$ but greater than that of $HfCl_4$, it is much greater than that of actinide tetrachlorides [104]Br_4 is more volatile than $HfBr_4$ (though the bromide is less volatile than the chloride) This extra volatility has been attributed to relativistic effects (though such enhanced volatility has not been observed with the halides of element 105)

8.2 Element 105[22,27—30]

The aqua ion of element 105 is readily hydrolysed,[27] even in strong HNO_3 and adheres to glass surfaces as do Nb^V, Ta^V and Pa^V, the +4 ions of the Group IV elements do not do this so this is an argument in favour of the +5 oxidation state Elution of element 105 as the α-hydroxybutyrate complex from cation exchange resins shows it to be eluted rapidly, like Nb^V, Ta^V and Pa^V but unlike Zr^{4+} and Eu^{3+} ions which are strongly retained on the column, again indication of an element in the +5 oxidation state Study of complex formation in HCl indicates resemblance to Nb^V and Pa^V rather than Ta^V It also differs from Ta in its fluoride complexes It has been suggested that at high HCl concentration a complex $\{[105]OCl_5\}^{2-}$ will exist[28] (this is a resemblance to Nb and Ta) Study of the volatility of the halides (assumed to be pentahalides) indicates that [105]Br_5 is less volatile than $NbBr_5$ and $TaBr_5$ (in contradiction of recent theoretical predictions) and [104]Br_4 The chloride appears to be more volatile than the bromide At present, it still remains to be confirmed that it was the binary halides studied in these experiments rather than oxyhalides, as well as confirming the oxidation state of the element since 105 would also be expected to exhibit a stable +4 state

To summarize, the evidence indicates that elements 104 and 105 most resemble elements in Groups IV (4) and V (5) respectively of the Periodic Table, as members of a 6d transition series, though sometimes resemblance to early actinides are noted One factor responsible for properties not matching those predicted by simple extrapolation is the so-called 'relativistic effect,' deviation from experimental behaviour caused by the high velocity (tending towards the velocity of light) of electrons in heavy atoms with highly charged nuclei [31]

9 Electronic Structure of the Elements

The ground-state configurations for the gaseous atoms have been obtained using Dirac–Fock calculations and are given in Table 3 There have been claims that relativistic effects may cause the contraction and stabilization of the $7p_{1/2}$ orbital so that it enters the valence shell around element 104, so that element 104 has the configuration [Rn]$5f^{14}$ $6d^1$ $7s^2$ $7p_{1/2}^1$ There is, however, no evidence for this

10 Predicted Chemistry[8,32—34]

10.1 Predicted Properties of Elements 104—112

10 1 1 Element 104

As the electron configuration is predicted to be [Rn]$5f^{14}$ $6d^2$ $7s^2$, the most probable oxidation state is +4 in aqueous solution Properties are likely to be similar to those of Zr and Hf, there is expected to be some chemistry in the +3 state too

10 1 2 Element 105

As the electron configuration is predicted to be [Rn]$5f^{14}$ $6d^3$ $7s^2$, the most probable oxidation state is +5 in aqueous solution Properties are likely to be similar to those of Nb and Ta, with some +3, +4 compounds too

Though no chemistry has yet been reported on elements with $Z > 105$, various predictions have been made Since the elements from 104 to 112 are believed to involve filling the 6d subshell, their properties are predicted to be those of transition metals

10 1 3 Element 106

Its properties are likely to be similar to those of Mo and W with a wide variety of complex ions The most stable oxidation state in aqueous solution has been suggested to be +4, though complex formation could make higher oxidation states such as +6 more stable From the point of view of identifying the elements by thermochromatography, volatile halides like a [106]F_6 would be useful Other volatile halides might include [106]Cl_6, [106]Cl_5 and [106]OCl_3 Recent relativistic calculations on [106]$(CO)_6$ suggest that it would be more stable than $U(CO)_6$ and have very similar bonding to the Cr and W analogues [35]

10 1 4 Element 107

Its properties are likely to be similar to those of Re, forming a wide variety of complex ions The most stable oxidation states in aqueous solution have variously been suggested to be +7 or +5 or +3, maybe higher due to complex formation Volatile higher fluorides like [107]F_6 would be expected

Table 3 Electronic structure of elements 104—121[a]

Element	6d	7s	$7p_{1/2}$	$7p_{3/2}$	8s	$7d^b$
104	2	2				
105	3	2				
106	4	2				
107	5	2				
108	6	2				
109	7	2				
110	8	2				
111	9	2				
112	10	2				
113	10	2	1			
114	10	2	2			
115	10	2	2	1		
116	10	2	2	2		
117	10	2	2	3		
118	10	2	2	4		
119	10	2	2	4	1	
120	10	2	2	4	2	
121	10	2	2	4	2	1

The electron configurations are given outside of the core [Rn] $5f^{14}$ [b] or $8p_{1\,2}$

Table 4 Predicted properties of elements 104—112

	104	105	106	107	108	109	110	111	112
Periodic Table Group	4	5	6	7	8	9	10	11	12
Main oxidation state	4	5	4	3	4	3	2	3	2
Other states	3	4	6	5, 7	3, 6, 8	1, 6	4, 6, 8		
E_I/eV	5 1	6 6	7 6	6 9	6 9	8 7	9 6	10 5	11 4
Redox potential/V	−1 8	−0 8	−0 6	0 1	0 4	0 8	1 7	1 9	2 1
Ionic radius/Å	0 71 (+4)	0 68 (+5)	0 86 (+4)	0 83 (+5)	0 8 (+4)	0 83 (+3)	0 80 (+2)	0 76 (+3)	0 75 (+2)
Atomic radius/Å	1 5	1 39	1 32	1 28	1 26				
M p , *T*/K	2400								
B p , *T*/K	5800								

Table 5 Predicted properties of elements 113—120

	113	114	115	116	117	118	119	120
Periodic Table Group	13	14	15	16	17	18	1	2
Main oxidation state	1	2	1	2	3	0	1	3
Other states			3	4	1,5	2,4,6,8	2	6
E_i/eV	7.4	8.5	5.2	6.6	7.6	8.7	4.8	
Redox potential/V	0.6	0.9	−1.5	0.1			−2.7	−3
Ionic radius/Å	1.4	1.2	1.5				1.8	1.6
Atomic radius/Å	1.7	1.6	2					
M.p., T/K	700	340	700			258		
B.p., T/K	1400	420	1400			263		

10.1.5 Element 108

As eka-osmium, a volatile tetroxide $[108]O_4$ would be expected. The most probable oxidation state in aqueous solution has been suggested to be +4, though it could be higher in oxyanions, *e.g.* +6, +8. As for osmium, a wide variety of complex ions are expected.

10.1.6 Element 109

The properties of this element are likely to resemble those of Ir, with a range of complexes. Hence the most probable oxidation state in aqueous solution could be +3 though oxyanions in higher states like +4 and +6 may be possible. A fluoride $[109]F_6$ would be expected to be highly volatile though other fluorides like $[109]F_7$ might be possible.

10.1.7 Element 110

Eka-platinum would be expected to form compounds in the +2 and +4 oxidation states. The +2 state has been suggested for the aqua ion, though others have calculated that the +6 and +8 states could be unexpectedly stable. It has been suggested that $[110]F_6$ could have similar stability to that of PtF_6.

10.1.8 Element 111

Detailed predictions have been made for eka-gold.[36] ΔH_{subl} is expected to be rather similar to that for gold. It is likely to be about as reactive as gold and most stable in the +3 state with a chemistry similar to that of Au^{III}, though possibly with more extensive complex ion formation. There is a possibility of a $[111]^{1}$ ion. The +1 state could be less important than for gold, but the +2 state will probably be unstable. MO calculations[37] applied to the actinides and transactinides predict an actinide contraction with element 111 having a smaller atomic radius than that of Cu, Ag or Au.

10.1.9 Element 112

Eka-mercury is predicted to be a noble metal. Simple extrapolation of boiling point for the elements above it in its Group suggests that it could be a liquid at room temperature. On the basis of a predicted high ionization energy and relativistic effects stabilising the $7s^2$ configuration, it could even be a gas. The +1 oxidation state is predicted to be most important, though higher states like +2 could be important too. It is likely to be a 'soft acid' forming stable complexes.

10.2 Predicted properties of Elements 113—120

To predict the properties of elements 113 onwards, the electron configurations shown in Table 3 are used, assuming that for the elements 113—118 the 7p orbitals are filled, elements 119—120 involve filling the 8s orbital, whilst from 121 to 153, one electron is first placed in the 7d (or 8p) orbital then the 5g and 6f orbitals

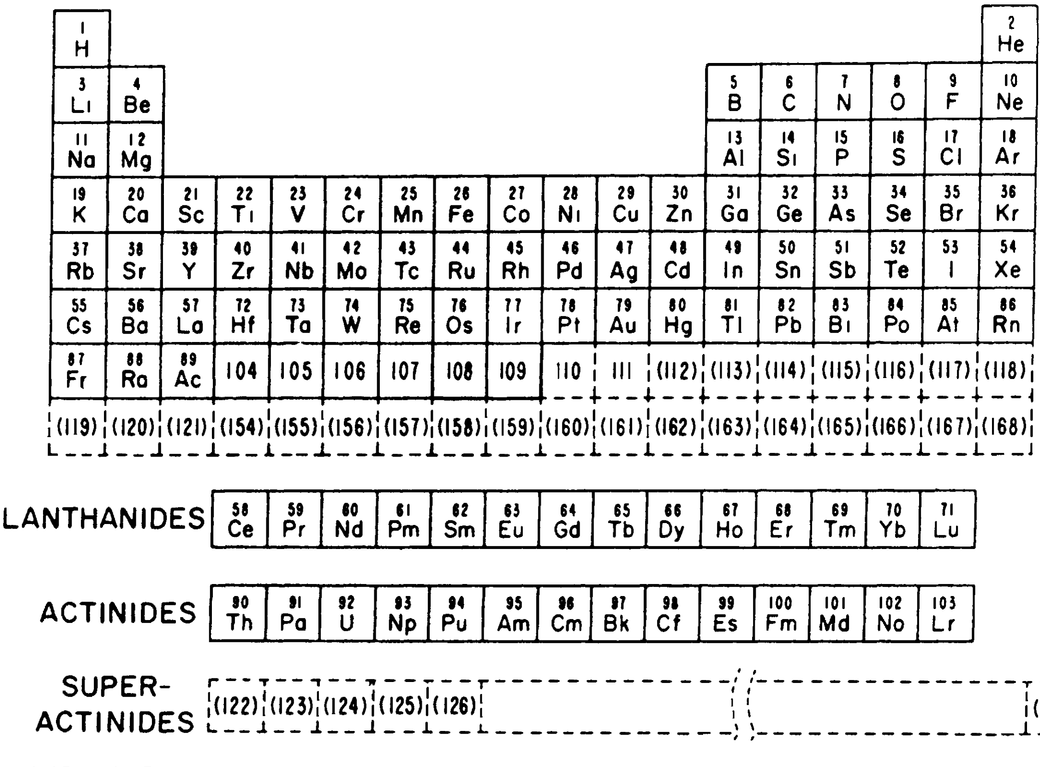

Figure 7 Extended Periodic Table (Adapted from G T Seaborg and W D Loveland, *The Elements beyond Uranium*, Wiley New York, 1990)

10 2 1 Element 113

Predicted melting and boiling points of 430 and 1130 °C were obtained by considering[38] the properties of the lighter elements in the group then extrapolating Its main oxidation state was predicted to be + 1 owing to the increased stability of the 7s electrons It will resemble Ag rather than Tl, thus [113]Cl is expected to be soluble in HCl and ammonia It will form stronger complexes than Tl

Table 6 Melting and boiling points of the Group III elements

Element	Ga	In	Tl	113
M p , *T*/°C	30	157	303	430 (est)
B p , *T*/°C	2403	2080	1457	1130 (est)

10 2 2 Element 114

Element 114 is predicted to have an unexpectedly low boiling point, a relativistic effect, this would be due to the stability of the $7p_{1/2}^2$ sub-shell It is predicted to be a rather noble metal Its chemistry would be largely of the +2 state, resembling lead in its chemistry, forming an insoluble chloride and sulfate but a soluble nitrate and acetate Its complexes would be stronger than those of lead

Table 7 Melting and boiling points of the Group IV elements

Element	Ge	Sn	Pb	114
M p , *T*/°C	945	232	327	70 (est)
B p , *T*/°C	2850	2623	1751	150 (est)

10 2 3 Element 115

A Group VB element, it is predicted to have a stable + 1 oxidation state, owing to a relativistic splitting between the $7p_{1/2}^2$ and $7p_{3/2}^1$ orbitals, making $7p_{1/2}^2$ a stable 'filled shell ' It is predicted to have a chemistry similar to that of Tl^+

10 2 4 Element 116

Extrapolating from polonium, its most stable oxidation state is predicted to be +2, with some chemistry in the +4 state Some calculations imply that it could be considerably more electropositive than Table 5 suggests [39]

10 2 5 Element 117

This element is expected to have some metallic proprieties, following the trend on descending the halogen series In keeping with this, instead of adopting the − 1 state characteristic of halogens it will predominately show +3, +5 and +7 states Its $7p_{1/2}^2$ $7p_{3/2}^3$ configuration, with $7p_{1/2}^2$ a stable 'filled shell,' could lead to a considerable chemistry in the +3 state It could also form interhalogen compounds with F, Cl, Br and I

10 2 6 Element 118

On account of its closed outer shell, element 118 is predicted to be a noble gas but the most electropositive of them, following the Group trend Examining the trends in melting and boiling point (Table 8), it can be seen that there is the possibility of 118 being a 'noble liquid' It would be expected to have a similar chemistry to that of xenon, but be more reactive, thus fluorides might include $[118]F_2$, with some ionic character, and also a tetrafluoride $[118]F_4$ and oxide $[118]O_4$

Table 8 Melting and boiling points of the Group 0 elements

Element	Ar	Kr	Xe	Rn	118
M p , *T*/°C	−189	−157	−112	−71	−15 (est)
B p , *T*/°C	−186	−153	−108	−62	−10 (est)

10 2 7 Element 119

This is expected to be an alkali metal, showing a + 1 oxidation state The 8s electron may have a high ionization energy so that its redox potential could be higher than expected by extrapolation Its chemistry could thus bear a closer resemblance to K rather than to Cs, with metallic and ionic radii smaller than expected If core p electrons could be removed, it could exhibit higher oxidation states than + 1

10 2 8 Element 120

This is expected to be an alkaline earth metal, +2 oxidation state As for element 119, a higher redox potential than predicted by extrapolation is possible Element 120 would be expected to resemble Ca or Sr in the +2 state, with higher oxidation states possible if p electrons could be removed

10 2 9 Element 121

This is predicted to be resemble La and Ac It marks the start of a long transition series in which the 6f and 5g orbitals are used that has been termed the Superactinides

11 Future Discoveries

Apart from the continuing attempts to synthesize elements with atomic numbers greater than 111, further studies on the chemistry of elements 104 and 105 should disclose more than one oxidation state, particularly for element 105 Definite confirmation of the assumed oxidation states of 104 and 105 is awaited It should now be possible to carry out chemical experiments with element 106 using the newly discovered more stable isotopes of masses 265 and 266 By analogy with tungsten (its 5d homologue) 106 would be expected to form volatile halides like $[106]F_6$ If more stable, neutron-rich isotopes of elements 107—111, expected to have longer half-lives, can be synthesized, chemical studies may be possible

12 Note added in proof

Two atoms of element 112 have been reported to result from the reaction of ^{208}Pb with ^{70}Zn, it is an α-emitter with a halflife of 240 (+430, −90) μs

$$^{208}Pb + ^{70}Zn \rightarrow ^{277}[112] + 1_n$$

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