

Superheavy Elements

A Prediction of Their Chemical and Physical Properties

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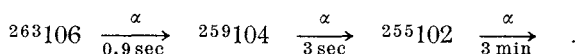
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I. Introduction

Very recently *Oganesian*, *Flerov* and coworkers (1) in Dubna announced the discovery of element 106. Although they observed less than 100 fission tracks of the decaying nuclei of this element, formed after the heavy-ion bombardment of Crions on Pb, they were able to measure a half-life of about 20 msec for one isotope and 7 msec for another. At about the same time *Ghiorso* and coworkers (2) in Berkeley found a new alpha activity for which they established the genetic link with the previously identified daughter and grand-daughter nuclides



This evidence indicates that a new element has been added to the periodic table, thus presenting a new challenge to scientists.

Until 1940 the heaviest known element was uranium with the atomic number 92, and at that time (about 1944) the actinide concept of *Seaborg* (3) was just a hypothesis. It is thus apparent that great progress has been made since then. Fourteen new elements have been added to the periodic system and much chemical and physical information has been gathered concerning this region of elements. Hence we can expect that element 106 is probably not the last element but only a step toward an even longer periodic table. The approach used in the experiments up to now to produce even heavier transuranium elements has been to proceed element by element into the region of atomic numbers just beyond the heaviest known by bombarding high-*Z* atoms with small-*Z* atoms. There have been very difficult and laborious attempts to proceed even further (4, 5). The upper limit of this method is determined by experimental feasibility; it cannot now be predicted with certainty but will be about element 108 or 109. The other way to proceed is to bombard two very heavy elements with each other, thus producing superheavy elements directly. This method will probably overlap with the first method at its lower end.

This second method, which must be the result of bombardments with relatively high *Z* heavy ions, is still in preparation at several places in the world, *i. e.* Dubna in the USSR, Berkeley in the USA, Orsay in France, and Darmstadt in Germany. If this method is successful, it should lead to the nearly simultaneous discovery of a number of new elements.

There is general agreement that theoretical predictions of nuclear stability, which we discuss briefly in the next paragraph, define a range of superheavy elements with sufficiently long half-lives to allow their study, provided they can be synthesized. What cannot be predicted is whether there exist nuclear reactions for such synthesis in detectable amounts on earth.

The known elements heavier than uranium are usually called by the very unspecific name of transuranium elements. In the upper range this term is ex-

pected to overlap with the equally ill-defined expression superheavy elements. To clarify the situation from a nuclear physics point of view, one may define the end of the transuranium elements and the beginning of the superheavy elements as the element where the nuclear stability of the longest-lived isotope increases again with increasing Z . The observed strong decrease of the half-lives of the transuranium elements known up to now can be seen in Fig. 1. The question is where and if this trend to even smaller half-lives is likely to end.

From a chemical point of view the elements, including the unknown superheavy elements, are well defined by their location in the periodic table. The elements up to 103 are the actinides or the $5f$ transition elements. Chemical reviews of these are given by *Seaborg* (6, 7), *Cunningham* (8), *Asprey* and *Pennemann* (9), and *Keller* (10). The $6d$ transition series starts with element 104. Of course, the first chemical question to be answered is whether this simple series concept of the periodic table still holds for the superheavy elements. A very comprehensive review of elements 101 to 105, discussing the nuclear stability and chemical behavior of the predicted elements, was given by *Seaborg* (5) in 1968. Several other articles dealing mainly with the chemical behavior of superheavy elements, the search for superheavy elements in nature, and the electronic structure of these elements have since been published. The references are given in the discussion below.

In this summary of the very quickly developing field of the superheavy elements, the main emphasis lies on the prediction of their chemical properties. Apart from the general interest of the question, this knowledge is expected to be very important because chemical separation will be one of the methods used to detect superheavy elements.

II. Predictions of Nuclear Stability

Like the well-known effect of the closed shells in the atomic electron cloud at $Z = 2, 10, 18, 36, 54, 86$, which is the physical basis for the structure of the periodic table, the effect of closed nucleon shells together with a large separation to the next unoccupied shell also makes for considerable nuclear stability. The nucleus consists of two kinds of particles, protons and neutrons, so that we have two series of so-called magic numbers. These are for protons 2, 8, 20, 28, 50, 82, and for neutrons 2, 8, 20, 28, 50, 82, and 126. Nuclei where both protons and neutrons are magic, (^{16}O , ^{40}Ca or ^{208}Pb , for example) are called double-magic nuclei and are particularly stable. As we go to even heavier nuclei, the effect which most heavily influences stability to α -decay or fission (the most important decay modes) is the increasingly large repulsion of the nucleonic charges against the attractive nuclear forces, which severely shortens the half-lives of the nuclei (17), as can be seen from Fig. 1. This suggests the question: Is the stabilizing effect of the next

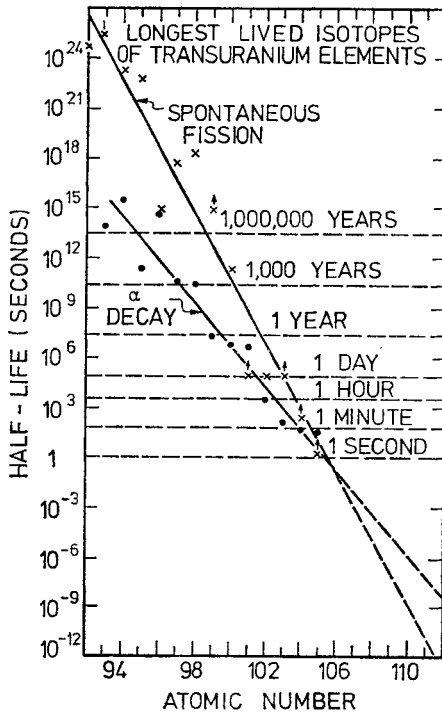


Fig. 1. The longest-lived isotopes of transuranium elements as a function of Z for spontaneous fission and α decay (17)

double-magic configuration large enough to counteract this repulsion and to lengthen the half-lives yet again?

Because it was assumed that the next protonic magic number was 126 (by analogy with the neutrons), early studies of possible superheavy elements did not receive much attention (12–15), since the predicted region was too far away to be reached with the nuclear reactions available at that time. Moreover, the existence of such nuclei in nature was not then considered possible. The situation changed in 1966 when *Meldner* and *Röper* (16, 17) predicted that the next proton shell closure would occur at atomic number 114, and when *Myers* and *Swiatecki* (18) estimated that the stability fission of a superheavy nucleus with closed proton and neutron shells might be comparable to or even higher than that of many heavy nuclei.

These results stimulated extensive theoretical studies on the nuclear properties of superheavy elements (19). The calculations published so far have been based on a variety of approaches. Most calculations were performed by using a phenomenological description within the deformed shell model (20–23). In this model the nucleons are considered to move in an average potential and the shape of the potential and other parameters are chosen by fitting single-particle levels in well-investigated spherical or deformed nuclei. Regardless of the approach followed, the authors agree in predicting a double-magic nucleus $^{298}114$, although several other magic proton and neutron numbers near these values have been discussed.

There are also several self-consistent calculations (17, 24–27) but suitable parameters have to be used, because the nucleon-nucleon force is not known from general considerations. Most authors also accept the magic numbers $Z = 114$ and $N = 184$.

In addition to the proton magic number 114, a second superheavy magic proton number was investigated at $Z = 164$ (23, 28). Although the realization of such a nucleus seems to be far from any practical possibility at the moment, one should bear this region in mind because many most interesting questions could be answered if it were possible to produce these elements. One way to actually proceed

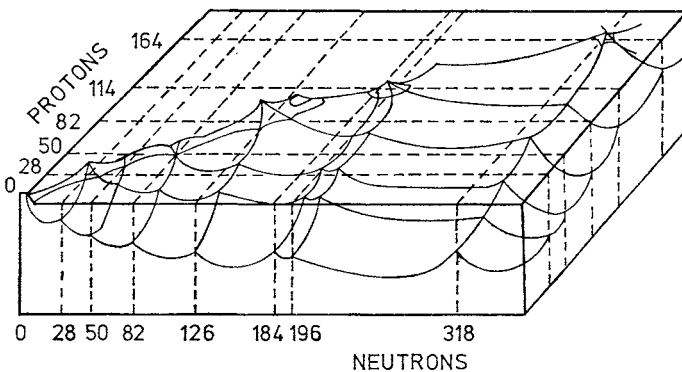


Fig. 2. Schematic drawing of the stability of the nuclei as a function of the number of protons and neutrons. The expected islands of stability can be seen near $Z = 114$ and $Z = 164$ (29)

into this region is the observation of the X-rays from the quasi-molecular systems which are transiently formed during heavy ion collision (109).

These predictions are depicted very schematically in Fig. 2 in an allegorical fashion (29). The long peninsula corresponds to the region of known nuclei. The grid lines represent the magic numbers of protons (Z) and neutrons (N). The third dimension represents the stability. The magic numbers are shown as ridges and the double-magic nuclei, like ^{208}Pb , are represented as mountains. The two regions near $Z = 114$ and $Z = 164$ show up in Fig. 2 as "islands of stability" within the large "sea of instability".

The detailed calculations quoted above predict potential barriers against fission, *i.e.* the total energy of the nucleus is calculated as a function of the deformation, because a deformation parameter describes at the one extreme the spherical nucleus and at the other the two separated nuclei after fission. All of these calculations indicate a maximum (or two) at a small deformation, whereas we get a dip of a few MeV at zero deformation and a trough of a few hundred MeV for very large deformations. The result of such a calculation is shown in Fig. 3

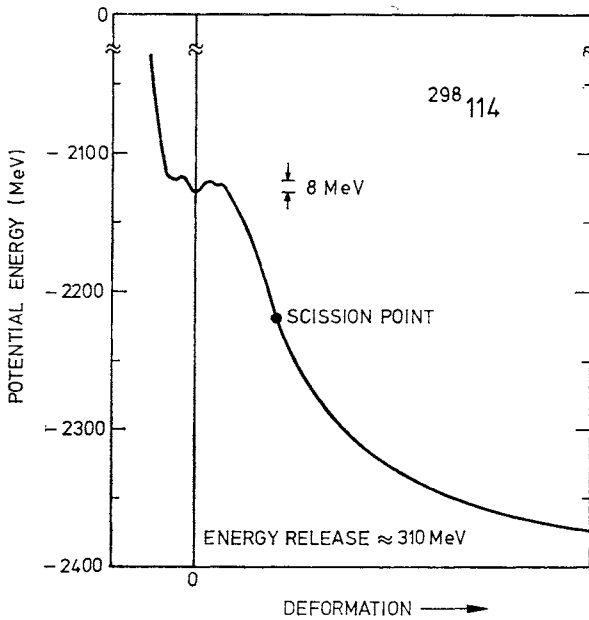


Fig. 3. Total energy as a function of the deformation of the expected double-magic nucleus $^{298}_{114}\text{Pb}$. The small minimum at the deformation zero is expected to be the reason for the very long lifetime of this nucleus (32)

for the expected double-magic nucleus $^{298}_{114}\text{Pb}$. This small minimum at zero deformation plays an important role; it keeps the nucleus in spherical shape and prevents rapid decay in the fission path. Spontaneous fission can occur only by the extremely slow process of tunneling through the several MeV high barrier.

Thus, the height and width of this barrier play a most important role in the prediction of the half-lives against fission (37). For the double-magic nucleus $^{298}114$ a height of between 9 and 14 MeV is predicted, depending on the method used. This yields spontaneous fission half-lives of between 10^7 and 10^{15} years.

These first results were very promising and stimulated a very extensive but up to now unsuccessful search for superheavy elements in nature. A most comprehensive review of this subject was given by *G. Herrmann* (32). But, besides spontaneous fission, a nucleus can decay by other decay modes like α decay, β decay, or electron capture. The most comprehensive study of half-lives in the first superheavy island was performed by *Fiset and Nix* (33). Figure 4 is taken from their work.

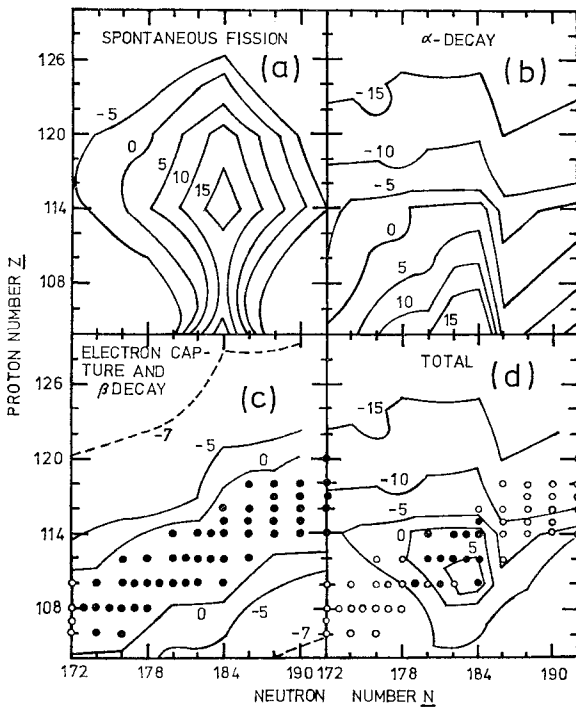


Fig. 4. Summary of predictions of the half-lives of the nuclei at the first island of stability. (a) spontaneous-fission half-lives, (b) α -decay half-lives, (c) electron-capture and β -decay half-lives, and (d) total half-lives. The numbers give the exponent of 10 of the half-lives in years (33)

The results show that, as one moves away from the double closed-shell nucleus $^{298}114$, the calculated spontaneous fission half-lives in Fig. 4a decrease from 10^{15} y for nuclei on the inner contour to 10^{-5} y (about 5 min) for nuclei on the outer contour. With respect to spontaneous fission, the island of superheavy nuclei is a mountain ridge running north and south, with the descent being most gentle in the northwest direction. The calculated α -decay half-lives in Fig. 4b, however,

decrease, rather smoothly with increasing proton number from 10^5 y for nuclei along the bottom contour to 10^{-15} y (about 30 nsec) for nuclei along the top contour. The discontinuities arise from shell effects. The β -stability valley crosses the island from the southwest to the northeast direction.

The calculated β -decay and electron-capture half-lives in Fig. 4c decrease from 1 y for nuclei along the inner contour to 10^{-7} y (about 3 sec) for nuclei at the outer contour. The total half-lives in Fig. 4d are obtained by taking into account all three decay modes. The longest total half-life of 10^9 years is found for the nucleus $^{294}110$. A three-dimensional plot of these results (35) is given in Fig. 5, where the island character of this region of relative stability is beautifully demonstrated.

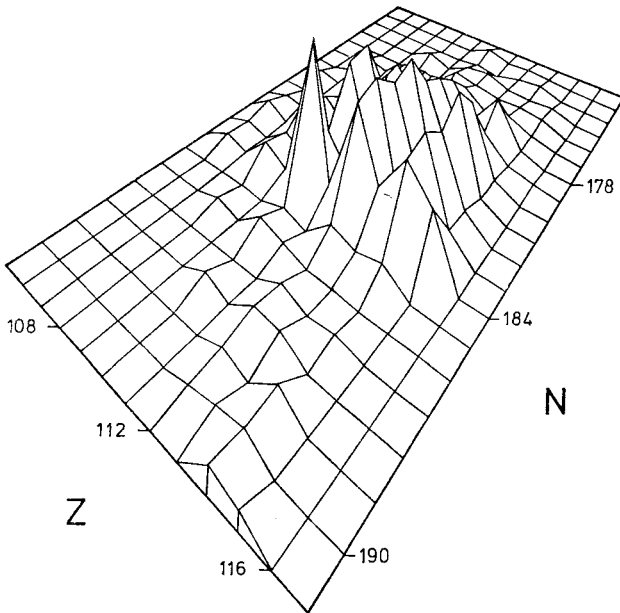


Fig. 5. Same as Fig. 4d in a three-dimensional plot (35)

In considering such results (34), one should be aware of the great uncertainties associated with the extrapolation of nuclear properties into the unknown region. The calculations are associated with large errors. The total uncertainty for all three decay modes discussed here is as large as 10^{10} for the half-lives.

The half-lives for the second island of stability are even smaller. In the most optimistic estimates, they are not more than a few hours, and the uncertainty of 10^{10} brings them down into the region of nsec. The second assumption of course, which has still to be proved, is that these nuclei can in fact be produced.

In conclusion, one may say that there is general agreement that theoretical predictions of nuclear stability define a range of superheavy elements in the vicinity of element 114 with sufficiently long half-lives to allow their study, provided they can be synthesized.

90 to 103 following actinium. Since there were already in the known region of elements a few deviations from *Madelung's* simple rules, especially in the lanthanides and actinides, *Chaikorskii* (38) and later *Taube* (39) tried to predict these anticipated deviations. In Table 1 we show the predictions of *Gol'danskii*, *Seaborg*,

Table 1. Predictions of the ground-state configurations of *Gol'danskii* (37), *Chaikorskii* (38), *Taube* (39) and *Seaborg* (5) for elements 121 to 127 and 159 to 168, using the principle of the extrapolation within the periodic table. The main quantum numbers (5*g*, 6*f*, 7*d*, 8*s*) are not shown. This table is taken from *Mann* (35)

Element	<i>Taube</i> (39)	<i>Gol'danskii</i> (37)	<i>Seaborg</i> (57)	<i>Chaikorskii</i> (38)
121	ds^2	gs^2	ds^2	ds^2
122	fds^2	$g^2 s^2$	$g^2 s^2$	$d^2 s^2$
123	$gfds^2$	$g^3 s^2$	$g^3 s^2$	$d^3 s^2$
124	$g^2 fd s^2$	$g^4 s^2$	$g^4 s^2$	$f^2 d^2 s^2$
125	$g^3 f d s^2$	$g^5 s^2$	$g^5 s^2$	$g^2 f^2 ds^2$
126	$g^4 fd s^2$	$g^6 s^2$	$g^6 s^2$	$g^3 f^2 ds^2$
127	$g^5 fd s^2$	$g^7 s^2$	$g^7 s^2$	$g^5 d^2 s^2$
159	$d^7 s^2$	$d^7 s^2$		$d^7 s^2$
160	$d^8 s^2$	$d^8 s^2$		$d^9 s^1$
161	$d^9 s^2$	$d^9 s^2$		$d^{10} s^1$
162	$d^{10} s^2$	$d^{10} s^2$		$d^{10} s^2$
163–168	$8s^2 8p^n$ ($n = 1 - 6$) for all columns			

Chaikorskii and *Taube* for elements 121 to 127 and 159 to 168. Apart from small discrepancies in these somewhat uncertain regions, there was general agreement that the unfinished 8th row of the periodic table would be finished by the 6*d* elements ending at element 112 and the 7*p* elements at 118. From a conservative point of view, every extrapolation into the region starting with element 121 is expected to be very speculative. Nevertheless, the reliability of the location of the elements in the periodic table seems to be relatively unambiguous.

b) Ab-initio Atomic Calculations. The prediction of the electronic configurations of the superheavy elements became much more reliable when ab-initio atomic calculations became available and accurate enough to be used in the field of the superheavy elements.

In the following paragraph we give a very brief description of the principles used in the calculations. For the details, especially the exact formulas used, we refer to the literature. All the calculations that are useful in this connection are based on the calculation of the total energy E_T of the electronic system, given by the expression

$$E_T = \frac{\langle \psi | \mathbf{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

where ψ is the total wave function and \mathbf{H} the Hamiltonian of the system. The physical solution is found when E_T is at the total minimum after the variation of ψ .

Depending on the ansatz for the total wave functions ψ and the Hamiltonian \mathbf{H} of the system, this minimalization of the total energy leads to a set of different, usually coupled differential equations. The solution of these equations gives the total wave function and hence the total energy. These methods, usually called Hartree and Hartree-Fock methods, are described in detail in various texts and papers (40). For those planning to do such calculations, *R. D. Hartree's* "Calculation of Atomic Structure" (41), and "Atomic Structure Calculations" (42) by *F. Hermann* and *S. Skillman* are recommended. A review article by *I. P. Grant* (43) gives an excellent description of relativistic methods. A good summary is also given by *J. B. Mann* (35).

Let us discuss very briefly the various methods that have been used. The first group of calculations is done by using the non-relativistic Hamiltonian (ignoring spin-orbit interaction)

$$\mathbf{H} = - \sum_i \frac{1}{2} \nabla^2 - \sum_i \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} .$$

Here the first term with ∇ the Nabla operator is the kinetic energy, the second is the potential energy due to the nuclear charge, and the last term is the total electrostatic interaction energy over all pairs of electrons.

Hartree's method (H) considers the total wave function to be a product of one-electron wave functions $\psi = \prod_i \varphi_i$; this leads, after the variation of the total energy, to a set of second-order homogeneous differential equations that have to be solved for the radial wave functions of the electrons of each shell. The last term due to the interaction of the electrons is given by the potential generated by all the other electrons. In this respect the set of the differential equations is, of course, already coupled. This was the basic method used by *Larson et al.* (44) for the first atomic calculations in the region of superheavy elements $Z = 122$ to 127.

Hartree-Fock method (HF). Here the total wave function is assumed to be an antisymmetric sum of Hartree functions and can be represented by a Slater determinant

$$\psi = (N!)^{-\frac{1}{2}} |\varphi_1(1) \varphi_1(2) \dots \varphi_N(N)|$$

which automatically obeys the Pauli principle.

The effect of the determinantal wave function is to greatly complicate the resulting differential equations by adding exchange potential terms, giving rise to an inhomogeneous equation, for which the correct solutions becomes much more difficult and time-consuming. For the exact equations, see for example *J. B. Mann* (35). A program using this method was developed by *C. Froese-Fischer* (45).

Hartree-Fock-Slater method (HFS). In this method the inhomogeneous parts of the equations used in the Hartree-Fock method are approximated by a local

potential, as proposed in 1951 by Slater (46). This approximation yields much simpler homogeneous differential equations in which the potential terms are identical for every orbital of the atom, which makes the actual computation less time-consuming by a factor of about 5 to 10, although the results are nearly as good as with the Hartree-Fock method.

For heavy elements, all of the above non-relativistic methods become increasingly in error with increasing nuclear charge. Dirac (47) developed a relativistic Hamiltonian that is exact for a one-electron atom. It includes relativistic mass-velocity effects, an effect named after Darwin, and the very important interaction that arises between the magnetic moments of spin and orbital motion of the electron (called spin-orbit interaction). A completely correct form of the relativistic Hamiltonian for a many-electron atom has not yet been found. However, excellent results can be obtained by simply adding an electrostatic interaction potential of the form used in the non-relativistic method. This relativistic Hamiltonian has the form

$$\mathbf{H} = \sum_k \left(i c \alpha(k) \cdot \nabla(k) - \beta(k) c^2 - \frac{Z}{r_k} \right) + \sum_{k < j} \frac{1}{r_{kj}},$$

where α and β are 4×4 matrices and ∇ is the Nabla operator. Using the variational method in the same manner as before and taking a Slater determinant as the wave function, one obtains two sets of first-order inhomogeneous differential equations to be solved for all electrons of the atom. This most complicated version of atomic calculations is called the *relativistic Hartree-Fock method* or *Dirac-Fock method* (DF) (48). Various papers calculating the ground-state configurations of superheavy atoms by this method have been published since 1969 (49–51). A complete discussion is given by J. B. Mann (35).

These very complicated inhomogeneous coupled differential equations can again be simplified by using Slater's approximation. This method is therefore called the *relativistic Hartree-Fock-Slater* or *Dirac-Fock-Slater* (DFS) (52–53) calculations, and they have also been done by several authors for the superheavy elements (54–56).

The results for the ground-state configurations of all superheavy elements up to 172 and for element 184 are given in Table 2 (35, 50, 56–60). In only very few cases are the results different for the two best methods, DF and DFS, but the differences are so small that no final decision can be made.

The first difference that becomes obvious in comparison to the empirical continuation of the electron filling discussed above (29, 37–39) occurs at elements 110 and 111. The calculated ground-state is $s^2 d^8$ and $s^2 d^9$, respectively, which is not at all common in the homologs of the two elements.

Also, beginning with element 121, every element has a different ground-state configuration than that predicted by simple extrapolations. The main reason for this behavior is that, unexpectedly, an 8p electron state becomes occupied at element 121, and at least one of these electrons remains bound through all the following elements. In the 160 region the difference between the simple predictions and the results of the calculations is already so large that the position of the elements in the periodic table is changed drastically. (For an overview and com-

Table 2. Atomic ground-state configurations for the neutral elements 103 to 172 and 184 according to *Mann (35)* and *Fricke and Waber (85, 60)*, using self-consistent Dirac-Fock calculations

Element	Rn core + $5f^{14}$ +	Element	$Z = 120$ core +	Element	$Z = 120$ core + + $8p_{1/2}^2$ +	Element	$Z = 120$ core + + $8p_{1/2}^2 5g^{18} 6f^{14}$ +
103	$7s^2 7p$	121	$8p$	139	$5g^{13} 6f^2 7d^2$	157	$7d^3$
104	$7s^2 6d^2$	122	$8p 7d$	140	$5g^{14} 6f^3 7d^1$	158	$7d^4$
105	$7s^2 6d^3$	123	$8p 7d 6f$	141	$5g^{15} 6f^2 7d^2$	159	$7d^4 9s^1$
106	$7s^2 6d^4$	124	$8p 6f^3$	142	$5g^{16} 6f^2 7d^2$	160	$7d^5 9s^1$
107	$7s^2 6d^5$	125	$8p 6f^3 5g$	143	$5g^{17} 6f^2 7d^2$	161	$7d^6 9s^1$
108	$7s^2 6d^6$	126	$8p 7d 6f^2 5g^2$	144	$5g^{18} 6f^1 7d^3$	162	$7d^8$
109	$7s^2 6d^7$	127	$8p^2 6f^2 5g^3$	145	$5g^{18} 6f^3 7d^2$	163	$7d^9$
110	$7s^2 6d^8$	128	$8p^2 6f^2 5g^4$	146	$6f^4 7d^2$	164	$7d^{10}$
111	$7s^2 6d^9$	129	$8p^2 6f^2 5g^5$	147	$6f^5 7d^2$	165	$7d^{10} 9s^1$
112	$7s^2 6d^{10}$	130	$8p^2 6f^2 5g^6$	148	$6f^6 7d^2$	166	$7d^{10} 9s^2$
113	$7s^2 6d^{10} 7p$	131	$8p^2 6f^2 5g^7$	149	$6f^6 7d^3$	167	$7d^{10} 9s^2 9p_{1/2}^1$
114	$7s^2 6d^{10} 7p^2$	132	$8p^2 6f^2 5g^8$	150	$6f^6 7d^4$	168	$7d^{10} 9s^2 9p_{1/2}^2$
115	$7s^2 6d^{10} 7p^3$	133	$8p^2 6f^3 5g^8$	151	$6f^8 7d^3$	169	$7d^{10} 9s^2 9p_{1/2}^2 8p_{3/2}^1$
116	$7s^2 6d^{10} 7p^4$	134	$8p^2 6f^4 5g^8$	152	$6f^9 7d^3$	170	$7d^{10} 9s^2 9p_{1/2}^2 8p_{3/2}^2$
117	$7s^2 6d^{10} 7p^5$	135	$8p^2 6f^4 5g^9$	153	$6f^{11} 7d^2$	171	$7d^{10} 9s^2 9p_{1/2}^2 8p_{3/2}^3$
118	$7s^2 6d^{10} 7p^6$	136	$8p^2 6f^4 5g^{10}$	154	$6f^{12} 7d^2$	172	$7d^{10} 9s^2 9p_{1/2}^2 8p_{3/2}^4$
119	$7s^2 6d^{10} 7p^6 8s$	137	$8p^2 6f^3 7d 5g^{11}$	155	$6f^{13} 7d_5$		$Z = 172$ core +
120	$7s^2 6d^{10} 7p^6 8s^2$	138	$8p^2 6f^3 7d 5g^{12}$	156	$6f^{14} 7d^2$	184	$6g^5 7f^4 8d^3$

parison, see the periodic table in Fig. 21, incorporating the results of the prediction of the elements up to 172 taken from *Fricke et al.* (56)). This disagreement with the results expected from a simple continuation of the periodic table is of course, a result of the interpretation of the periodic system in terms of chemical behavior, but the primary reason is the surprising order of filling of the outer electron shells in this region.

If we try to proceed to even heavier elements, the calculations come to a halt at $Z = 174$ because at this element the 1s level reaches the negative continuum of the electrons at a binding energy of $2m_e c^2 = 1$ MeV and the calculation breaks down. To proceed further, *Fricke* (61) introduced a phenomenological description of the quantum-electrodynamical effects into the SCF calculations (60), which shifts the binding energies of the inner electrons back to lower values. Using this method, he was then able to study the electron configurations of the elements beyond $Z = 174$.

2. Trends of the Chemical and Physical Properties

The detailed and sophisticated calculations of the electronic-ground states of the atoms are very worthwhile as an important, though only the first step toward predicting the chemical and physical properties of superheavy elements, because chemistry consists not only of the properties of the atoms but also of the molecules and their behavior. Ab-initio calculations of molecules were introduced for small molecules and small Z , and the state of the art is still far away from the point that allows actual calculations of the chemical properties of superheavy molecules. A first step in this direction has been taken by *Averill et al.* (62), who calculated the wave function of $(110)\text{F}_8$ using a muffin-tin method.

a) Trends Emerging from the Calculations. Although we are not able to calculate the properties of superheavy molecules at the present time, the atomic calculations give us more than just the electronic structure of the neutral elements.

One has to bear in mind that two elements from the same chemical group, which often have the same outer electronic structure will be chemically and physically slightly different. This can be to some extent explained as the effect of their somewhat different sizes, changed ionization potential, and the different energies and radial distributions of the wave functions between analogous shells. These quantities are also determined directly by the atomic calculations. The size of the atom or ion correlates strongly with the principal maximum of the outermost electronic shell, as found by *Slater* (63), thus giving a first estimate of this important magnitude. Sometimes the expectation value of $\langle r \rangle$ of the outermost shell is used as the radius, but the agreement with experiment is not so good.

There is considerable agreement that the ionization potentials have to be calculated in the adiabatic approximation, in which it is assumed that during the removal of an electron sufficient time elapses for the other electrons to rearrange themselves, so that the ionization potential is given by the difference in total energy of the two calculations with m and $m-1$ electrons. The other method, taking the calculated energy eigenvalues (64), can only be used as an approximation to this physical quantity.

In the first part of the periodic table it is relatively easy to make the connection between these quantities and a chemical interpretation because of the few shells involved and their large separation. Moreover, the influence of the inner electron shells is rather small so that the outer electron configurations are very similar in the same chemical group at different periods. When we proceed to higher elements at the end of the periodic table, the number of shells increases, the binding energy of the last electrons decreases, and there is competition between shells; hence the influence of the inner electrons becomes more significant. This rather complex behavior is further complicated by the fact that relativistic effects now begin to be important and the coupling between the angular momenta of the electrons changes from LS to intermediate or $j-j$ coupling. All these effects and their relative influences are taken into account in the ab-initio calculations. Of course, to prove their reliability in the superheavy region of elements, they have to reproduce the complex structure and its relationship to chemical behavior in the known part of the periodic table, which in all cases is done for example for the groundstate configurations of the atoms. The main change due to relativistic effects is the splitting of all shells with $l \neq 0$ into two subshells with $j = l + 1/2$ and $j = l - 1/2$. This means that, for example the p state splits into the $p_{1/2}$ subshell

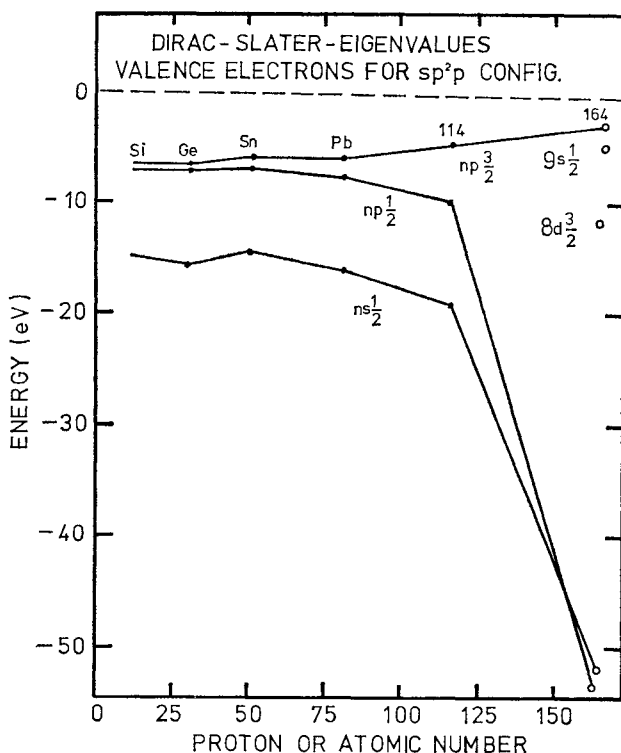


Fig. 7. Comparison of the eigenvalues of the ns , $np_{1/2}$ and $np_{3/2}$ electrons in the group-IVA elements using DFS calculations. This figure illustrates the very strong dependence of the spin-orbit splitting between the two p states as a function of the atomic number. For element 164, the $9s$ and $8d_{3/2}$ levels are also drawn (85)

with 2 electrons and the $p_{3/2}$ subshell with 4 electrons. How large this effect can be is apparent from Fig. 7, where the energy eigenvalues of the $p_{1/2}$ and $p_{3/2}$ electrons are plotted as a function of Z for the series of group-IV elements (65). This effect is of direct relevance for the chemical behavior of all elements in which these shells are the outer electron shells. This is, for example, the reason why in the group-IV elements the +2 valency becomes dominant for larger Z , as is already the case for lead, and why element 115 (eka-bismuth) is expected to have a monovalent state.

This spin-orbit stabilization also plays a dominant role in atomic lawrencium ($Z=103$) with probably (66) a ground-state $7s^2 7p_{1/2}^1$ instead of the expected $7s^2 6d^1$, and in all the elements beyond 120.

As a summary of the calculations Fig. 8 shows the energy eigenvalues of all outer electrons for all elements between $Z=100$ and 172 and in Fig. 9 the radii of the outermost electron wavefunctions for the elements 104 to 121 and 156 to 172 are shown.

In addition to the relativistic spin-orbit splitting, there are two more relativistic effects whose trends toward a chemical interpretation can be seen directly from the results of the calculations. The first is the so-called direct relativistic effect, which means the increase in the binding of the $s_{1/2}$ and $p_{1/2}$ levels relative to the nonrelativistic calculations. These s and $p_{1/2}$ levels, even for large main quantum numbers, have wave functions that are nonzero in the vicinity of the nucleus, where the potential is large and the relativistic effects are increasingly strong with increasing Z . This effect explains why the $7s$ electrons are so strongly bound at the end of the $6d$ transition series where, instead of the expected increased full $6d$ shell stability, the $7s^2$ electrons remain bound at the elements 110 and 111,

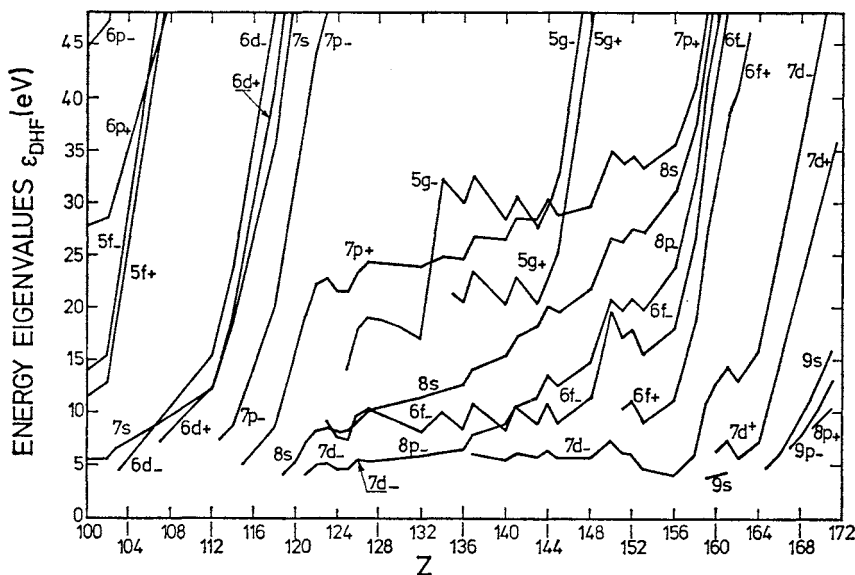


Fig. 8. Energy eigenvalues of the outer electrons for the elements 100 to 172 from DF calculations (35)

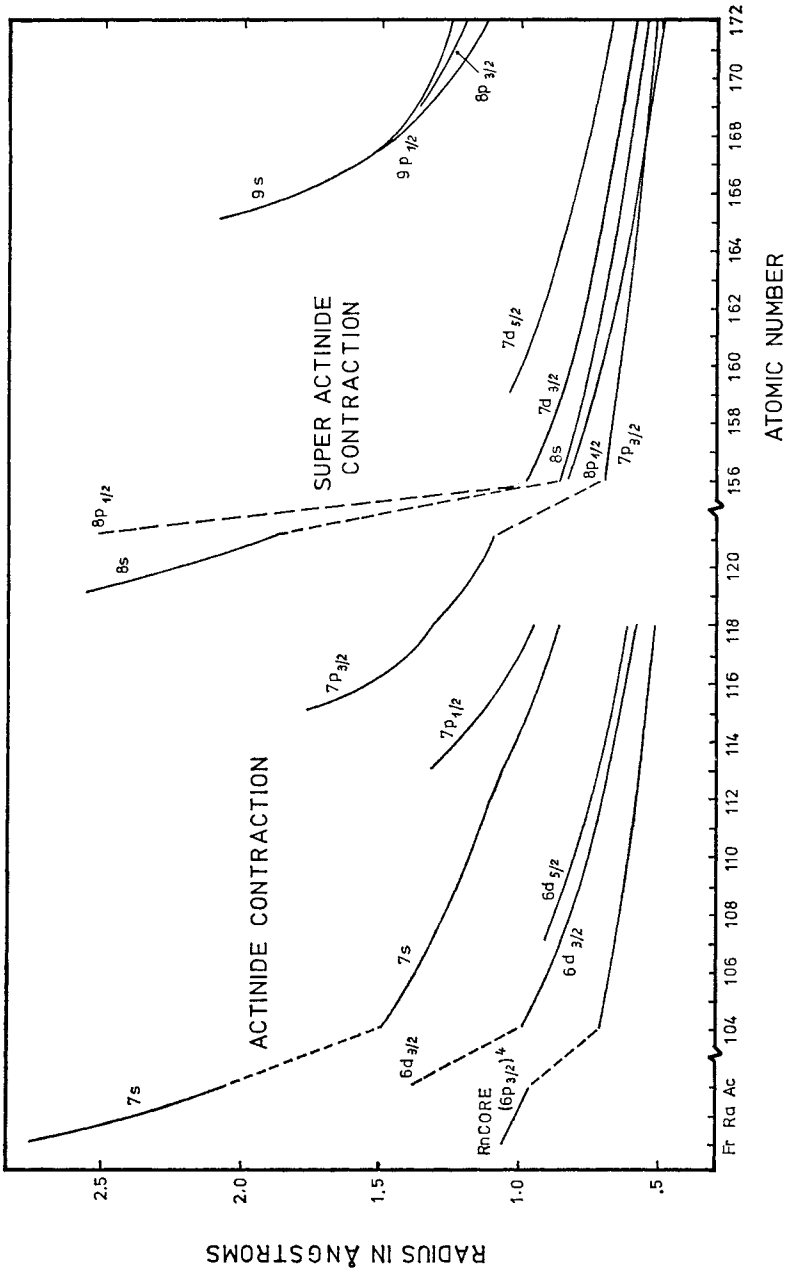


Fig. 9. The radii of the outer-electron wave functions for elements 104 to 121 and 156 to 172 from DFS calculations (67)

and possibly also at the ionized states of element 112, which would drastically change their chemical behavior relative to the extrapolated trends. This direct relativistic effect is also the reason why the trend of the decreased binding of the s electrons in the alkaline and alkaline earth metals stops at Fr and Ra, and the next metals of these groups are expected to have increased binding again. Parallel

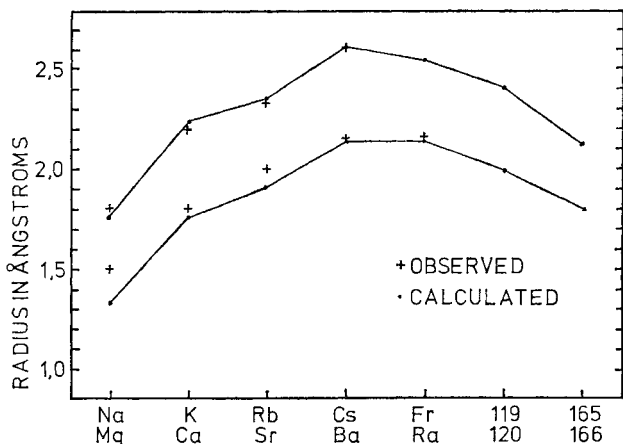


Fig. 10. Comparison of experimental and calculated atomic radii of the alkali and alkaline earth elements from DFS calculations (67)

to this result we show in Fig. 10 the calculated and experimental radii of these elements, taken from *Fricke et al.* (67), which shows excellent agreement. The conclusion from these calculations is that Cs is expected to be the largest atom in the entire periodic system, at least up to element 172.

The second relativistic effect to emerge from the results of the calculations is the so-called indirect relativistic effect. This effect describes the increased shielding and therefore decreased bonding of the electrons with large angular momentum, because the wave functions with small angular momentum are increased in binding and drawn into the atom because of the direct relativistic effect, thus shielding the other electrons more strongly. This effect is expected to occur, even from a chemical point of view, together with the large spin-orbit splitting effect at the end of the $7p$ elements at 118, where a noble gas element is actually located but a very reactive element with an easily obtainable $4+$ state would be expected because the last four $7p_{3/2}$ electrons are so loosely bound.

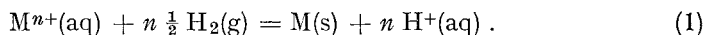
Now, we have seen in this discussion that it is possible to calculate quite a number of physical quantities, and we understand from these calculations that several trends are a result of some physical influences, but there is still a long way to go to the prediction of chemical properties. Even the calculated quantities cannot be used as absolute but only as relative numbers, and the calculated trends have to be scaled to the experimental values in the known part of the periodic table. Therefore *all* the predictions of all quantities can only be done by a combination of the traditional method of continuing the trends of the interesting physical and chemical quantities of a chemical group into the unknown region of elements with a comparison of the trends shown in the calculation, if this is possible. But although the calculations sometimes do not give absolutely correct values, they are necessary as a guide to an unknown region, because the overall nature of the elements is being changed by relativistic effects.

b) Empirical and Semi-empirical Methods. A chemist who is trying to separate, for example, an unknown element from a sample needs to know more than just that it is similar to element xy. For an experienced chemist it is sometimes enough to know the anticipated location of the unknown element in the periodic table, because of his feeling for trends within the periodic table. To a certain degree, this sort of hunch cannot be expressed in scientific terms nor can it be calculated by ab-initio methods. A good review of the loose connection between electron configuration and chemical behavior is given by *Jørgensen* (68).

The extrapolation of properties within either rows or groups of elements in the periodic table was and still is the best way of predicting the properties of unknown elements. There are quite a number of empirical and semi-empirical laws which have proved successful, ranging from the valence-bond theory (68), which must be used with care, via the Born-Haber cycle (69, 70) to *Jørgensen's* ingenious variations of this (71–73) to much more complicated extrapolations. For example, *David* (74) predicts thermodynamic quantities of the superheavy elements by plotting the log of the quantity versus the log of the atomic number. *Hoffmann* and *Bäcchmann* (75, 76a, 76b) used as plotting parameters for different properties Zv/x , Z/x and Zr^2/x , with Z the atomic number, v the atomic volume, x the electronegativity, and r the covalent radius of the central atoms. Their results seem to be fairly good but the theoretical justification for these methods is lacking. They were trying to predict the properties of compounds of superheavy elements, especially the methyl, ethyl, hydrides and chlorides. [For their results we refer to the references (75) and (76)]. This of course is, at least from a theoretical point of view, another order of magnitude more complex. They confirmed their results by comparing them with values from independent extrapolations or from experiments in the known region of elements (76b, 76c). *Eichler* (77) did similar extrapolations to obtain information on the thermochromatographic separation of superheavy elements and compounds, which is another possible way of detecting and separating superheavy elements in small quantities.

The rel-HFS and rel-HF computer programs allow calculations of electronic energy levels, ionization potentials, and radii of atoms and ions from hydrogen into the superheavy region. In order to arrive at the oxidation states most likely to be exhibited by each superheavy element and also the relative stabilities of these various oxidation states, we need to be able to relate these properties to calculable electronic properties. The relationship between reduction potentials and the Born-Haber cycle has offered an effective approach to this problem (69, 70).

Electrode potentials are usually related to the standard $H^+/\frac{1}{2}H_2$ couple, whose potential is set equal to zero. We therefore consider the change in state for reduction of the aqueous metallic cation, $M^{n+}(aq)$, to the metal, $M(s)$:



The change in Gibbs free energy is related to the reduction potential and to the enthalpy and entropy by the equation

$$- \Delta G = n E = - \Delta T + T \Delta S . \quad (2)$$

By considering all components in their standard states of unit activity or fugacity, we can obtain from these equations the standard electrode potential of the $M^{n+}/M(s)$ couple, as defined under the IUPAC Convention.

ΔS must be considered in each case, but so far, in most considerations pertinent to the superheavy region, it has either been chosen small or shown to be small (78). We shall therefore for simplicity consider only H° , which can be obtained through the Born-Haber cycle. First, the heat of sublimation, S_M , must be obtained through an extrapolation, preferably versus the row of the periodic tables, as has been done for several superheavy elements (*e.g.* for the discussion of elements 113 and 114). Secondly, the appropriate ionization energy, I_n , has to be calculated using ab-initio calculations. This value then has to be corrected, as discussed in the last paragraph. The difference between the calculated and experimental value in the known region of elements has to be extrapolated and then added to the calculated value.

The next part of the Born-Haber cycle is most conveniently taken to be the single-ion hydration energy, H_{Mn+} , although this quantity cannot be defined from a thermodynamic point of view. H_{Mn+} can be obtained by simple extrapolation or by calculation, using various empirical modifications of the Born equation, depending on circumstances. For example, *David* (74) used a simple extrapolation to obtain 75 kcal (g atom) $^{-1}$ for H_{113+} . *Keller et al.* (78) preferred to use the Born equation and obtained 72 kcal (g atom) $^{-1}$. These are then the quantities that make up ΔH° , that is, the heat of sublimation of the metal S_M , the ionization energy I_n , and the single-ion hydration energy H_{Mn+} . Since we are not considering the entropy, we have for the change in state (1)

$$-\frac{1}{n} \Delta H^\circ = E^\circ = \frac{1}{n} \left[(I_n + S_M + H_{Mn+}) - n \left(\frac{1}{2} D_{H_2} + I_H + H_{H+} \right) \right] \quad (3)$$

where $1/2 D_{H_2}$, half the dissociated energy of the hydrogen molecule, is 2.26 eV; I_H , the ionization energy of the hydrogen atom, is 13.59 eV, and we accept the single-ion hydration energy of the proton as -11.3 eV, the value derived by Halliwell and Nyburg (79). This yields a value of 4.5 eV for the energy released when one gram equivalent of hydrogen ions is combined with electrons.

Equation (3) can be used to calculate the standard electrode potentials. Calculations based on the Born-Haber cycle to obtain the relative stabilities of oxidation states are known as "Oxidation State Diagrams". These diagrams have been found useful in clarifying inorganic chemistry (69), even though their accuracy is sometimes low.

Jørgensen (71–73) has formulated an ingenious approach for predicting the stabilities of oxidation states, based on Eq. (3). If we consider one-electron changes only, Eq. (3) can be rewritten

$$I_n - [E^\circ + (\frac{1}{2} D_{H_2} + I_H + H_{H+})] = - (H_{Mn+} + S_M) \quad (4)$$

or

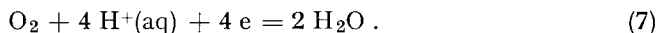
$$I_n - (E^\circ + 4.5) = - (H_{Mn+} + S_M) . \quad (5)$$

Jørgensen calls $(H_{Mn} + S_M)$ the “hydration difference”. $(E^\circ + 4.5)$ is given the symbol C_n and is called the “chemical ionization energy”. *Jørgensen* finds empirically that he can set the “hydration difference” equal to $(2n - 1)k$ so that

$$I_n - C_n = (2n - 1)k \quad (6)$$

where k is a parameter that *Jørgensen* has determined for various different types of elements.

Since he wishes to predict states in aqueous solution, *Jørgensen* next notes that the range of oxidation states must be limited to those that neither oxidize nor reduce water. The oxidation reaction usually encountered in acid solution is



The standard electrode potential, E° , is 1.23 volts for this half-reaction.

Therefore, any couple of E° larger than 1.23 volts can oxidize water, provided kinetic (“overvoltage”) effects are absent. Since, under these conditions, E° must be less than 1.23 volts, C_n must be less than 5.7 eV.

Jørgensen expresses the condition that the ion will not oxidize water as follows:

$$I_n - (2n - 1)k = C_n < 5.7 \text{ eV} . \quad (8)$$

On the other hand, from the thermodynamic point of view, any couple whose standard electrode (*i.e.* reduction) potential is negative will reduce water. *Jørgensen* writes this condition in the form appropriate to an oxidation reaction and obtains

$$I_{n+1} - (2n + 1)k = C_{n+1} > 4.5 \text{ eV} . \quad (9)$$

On occasion, it may be worthwhile recalling that the potential of water oxidation reaction (80), Eq. (7), is a function of pH and oxygen pressure

$$E = 1.23 - 0.059 \text{ pH} + 0.0148 \log P_{\text{O}_2} . \quad (10)$$

Similarly, the potential for water reduction reaction $[\text{H}^+(\text{aq}) + \text{e} = 1/2 \text{H}_2(\text{g})]$ is

$$E = - 0.059 \text{ pH} - 0.0295 \log P_{\text{H}_2} .$$

In applying *Jørgensen’s* approach, it should also be remembered that there are usually kinetic factors (so-called “overvoltage effects”) which results in hydrogen and oxygen being evolved only at potentials beyond the range of the thermodynamic ones (87). There is also often the question of the effect of complex ion formation.

Valence-bond theory has proven valuable in understanding the chemistry of the known elements (68). As in the case of any inexact theory, it must be applied to cases where it can be expected to have validity. Making comparable calculations for the known elements will give us an idea of the validity of valence-bond theory

for a specific superheavy element. We will not discuss this subject here in general, since details concerning the application of this method to the prediction of chemical properties may be found in the discussion of elements 111 and 115.

Another helpful scheme is the classification of ions with hard and soft Lewis acids by *Ahrland* (82) and *Pearson* (83). While a specific definition or scale of softness is not universally accepted, the general principles are clear. They can be used to give somewhat more information for predictions of what compounds or complex ions might be expected for the superheavy elements.

Hard Lewis acids are found among the small, highly charged ions such as Al^{+3} or La^{+3} , which have low-lying orbitals available for occupation — in general, these ions are not readily polarized. Soft Lewis acids tend to be large, easily polarized ions such as Ag^{+1} , and frequently the state of ionization is low. In addition, they contain unshared pairs of electrons such as *p* or *d* electrons in their valence shell. The hard Lewis bases are ions such as F^- or OH^- , which have small ionic radii and are characterized by high electronegativity and low polarizability and are difficult to oxidize. In comparison to these ions, I^- is more polarizable, acts as an electron donor and is therefore, a softer Lewis base.

Pearson's Hard-Soft-Acid-Base (HSAB) principle is that hard acid-base combinations form readily and are generally ionic compounds. The other group of stable compounds and complex ions involves the interaction between soft acid and soft bases. For these, the bonding is primarily covalent with interpenetrating orbitals. The combinations hard acid with soft base, or vice versa, have little stability.

Klopman (84) defined the frontier orbitals for a base as the highest occupied orbitals of the donor atom or ion and the lowest unoccupied orbitals of the acid or acceptor ion. For elements with low atomic numbers, such orbitals are radially extended, *e.g.* the $3d$ orbitals. With increasing atomic number this feature is not guaranteed, and orbitals that are not tightly bound may become buried beneath other competitive orbitals. The essential idea is that the frontier orbitals must overlap significantly before covalent bonding can occur in the soft-soft interactions.

The difference in the chemistry of the light and heavy actinides may be rationalized in this way. The early members beyond thorium have unpaired *d* and *f* electrons available for forming covalent bonds and hence, for example, they readily form many complex ions and intermetallic compounds. Such ions are soft acids. Beyond americium, the $5f$ electrons are not competitive and the closed shell of six $5f_{5/2}$ electrons will not be readily available for bonding, so that only those *f* electrons with $j=7/2$ are available. These tend to become buried radially as the atomic number increases and hence their divalent ions become relatively hard Lewis acids. These considerations are especially helpful in the region of superactinides because these elements do not have analogs in the known periodic table, where we have deeply buried but loosely bound $5g$ electrons.

IV. Discussion of the Elements

The use of the continuation of the periodic table, the predicted electronic configurations, and the trends which become obvious from the calculations plus the semiempirical and empirical methods, allows us to offer some detailed predictions of the properties of the elements beyond lawrencium ($Z = 103$) (85). Of course, these elements will first be produced at best on a "one atom at a time" basis, and they offer little hope of ultimate production in the macroscopic quantities that would be required to verify some of these predictions. However, many of the predicted specific macroscopic properties, as well as the more general properties predicted for the other elements, can still be useful in designing tracer experiments for the chemical identification of any of these elements that might be synthesized.

The most important property we need to know about an element is the stable oxidation states it can assume, because so many other chemical and physical properties depend upon the oxidation state. The second most important property to know concerns the relative stabilities of these oxidation states; that is to say, we need to know the standard electrode potential. As will be clear from the discussions in Section III.2b on this subject, the understanding of these two outstanding characteristics of the elements involves at least a knowledge of heats of sublimation, ionization potentials, ionic and atomic radii, and electronic energy levels. In this paragraph we try to focus on these properties, but we also summarize all the other properties so far predicted for the superheavy elements.

1. The $6d$ transition Elements $Z = 104$ to 112

Although elements 104, 105 (and very recently also 106) are known, they have not yet been much studied chemically. *Zvara* and coworkers (86) believe they have shown element 104 to be tetravalent but there is no confirmation from other experimental groups on this. A first discussion of the chemical separation of element 105 is also given by *Zvara* (87).

The electron configurations of the outer electrons of almost all the d -transition elements are given by the rule $(n-1) d^m n s^2$, where n is the number of the period (or the principal quantum number) and m goes from 1 to 10. This rule is not exactly valid in the 4th and 5th periods, where in some cases there is only one, or even no electron in the outer s shell. This behavior is well understood; both the increasing binding energy of the d electrons and the greater shielding of the s electrons with higher Z , as well as the stabilizing effect of the half-filled and filled d shell, lead to configurations where the number of ns electrons is less than two (88).

The main difference between the elements of the 4th and 5th periods and those of the 6th period is due to the fourteen $4f$ electrons, which are filled in between the occupation of the $6s^2$ and the $5d$ electrons. The filling of the $4f$ shell

shields the less penetrating $5d$ orbitals more effectively than the $6s$ because the d electrons are more fully barred from the inner parts of the atom by the centrifugal force $\frac{l(l+1)}{r^2}$. This means that the $d^m s^2$ configuration has increased stability in the 6th period, except at the high end where Pt and Au occur. This stabilizing effect of the $d^m s^2$ configuration becomes even larger in the next period, *i.e.* for the $6d$ elements, because the $7s$ electrons drop relatively deep into the atom. Thus they feel the very strong potential near the nucleus whereas the $6d$ electrons are shielded more strongly by the $5f$ electrons. Fig. 11 shows the calculated energy eigenvalues (56, 85) by a DFS method of the outer s and d electrons for the d transition elements of the 6th, 7th and 8th periods. The trend is clear: the s electrons are more strongly bound in the higher periods whereas the d electrons are lowered and, in addition, the d shell is split more and more into its two subshells, and the energy separation increases. Taken altogether, this explains why the electronic configuration of the neutral atoms of the transition elements in the 7th period will be given exactly by the rule $6d^m 7s^2$, as verified in the calculations shown in Table 2. The pairing energy that stabilizes filled and half-filled shells is no longer sufficient to break this general rule. Furthermore, pairing energy is as large as 1.1 eV per pair in the $3d$ elements and decreases for the higher periods. Cunningham (88) predicted this pairing energy to be less than 0.2 eV in the 7th period, so that its influence will be very small.

Fig. 12 shows the experimental first ionization energies of the transition elements for the $5d$ elements as well as the calculated values for the $5d$, $6d$, and $7d$ elements. This figure is located below Fig. 11 so that the trend of the ionization energy curves can be compared directly with the trend of the energy eigenvalues of the outer electrons. The ionization of the $5d$ electrons at the beginning of the $5d$ elements and the ionization of the $6s$ electrons at the end leads to the most stable configurations of the ion. The decrease in ionization energy between W and Re comes from the spin-orbit splitting. The $5d_{3/2}$ subshell, which holds only four electrons, is completed at W and the occupation of the less tightly bound $5d_{5/2}$ subshell begins with Re. The linear behavior thereafter is not continued for Pt and Au, where the $5d$ shell is closed sooner at the cost of the $6s$ electrons.

However, in the $6d$ elements the ionization of one $6d$ electron always leads to the most stable ion so that the ionization energy curve is nearly parallel to the energy eigenvalues of the most loosely bound $6d$ electron, as can be seen in Figs. 11 and 12. The calculated values are augmented by 0.2 eV, which equals the average difference between the experimental and calculated values for the 6th period. These values are expected to be correct to within ± 0.4 eV. (The values in Table 3 are taken for DF calculations.) But in ionic compounds first the $7s$ electrons, which are in the frontier orbital, have to be removed; their ionization energy is nearly 3 eV higher at the beginning and about 1 eV higher at the end of the $6d$ elements, which can also be seen in Fig. 12. Nevertheless, the relatively low ionization energy at the beginning of the $6d$ elements will be an indication that the maximal oxidation states for the $6d$ transition elements will be higher than, or at least equal to those in the $5d$ elements.

Cunningham (88) has given estimates of the sum of the first four ionization energies for elements 104 to 111. He uses extrapolation against the row of the

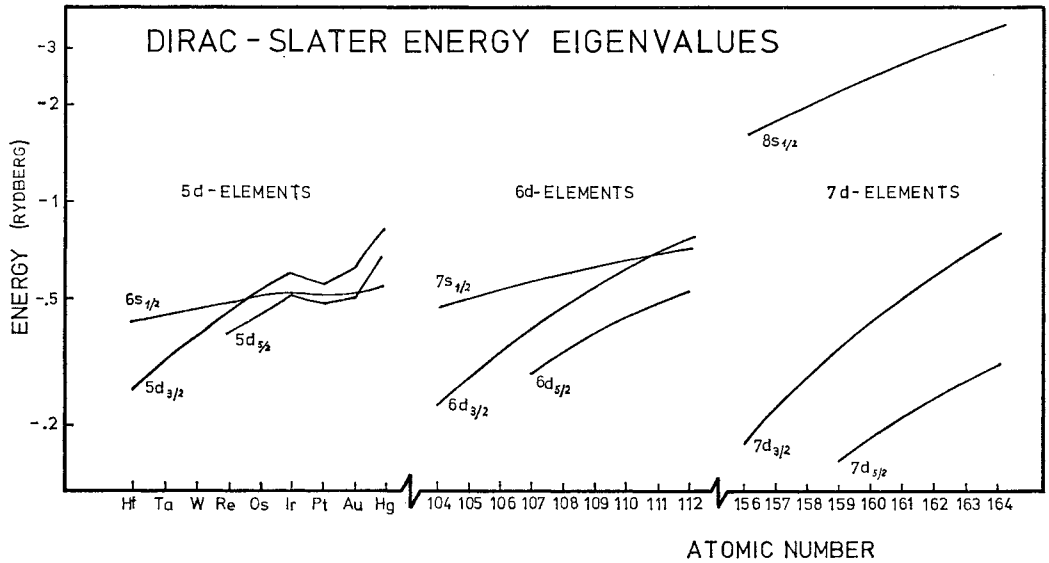


Fig. 11. Dirac-Slater (DFS) energy eigenvalues of the outer electrons for the $5d$, $6d$ and $7d$ elements. This shows the strong relativistic increase of the binding of the last s shell and the increase in the splitting of the d subshells (85)

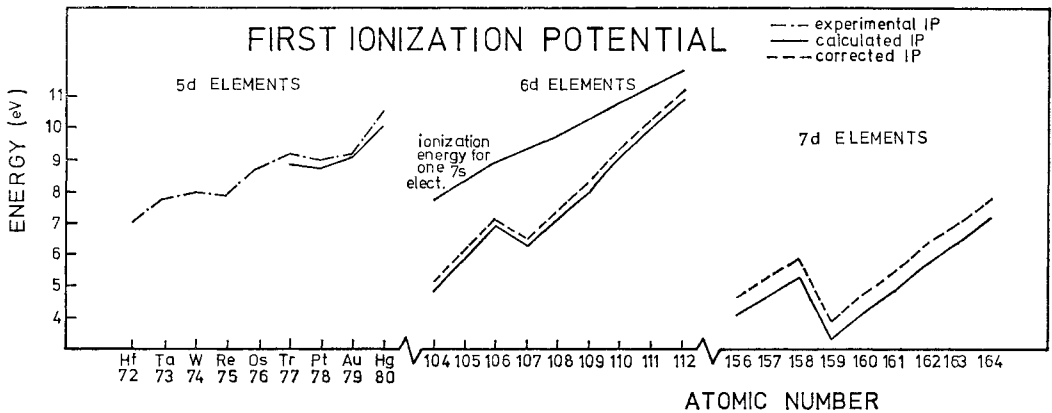


Fig. 12. First ionization energies for the $5d$, $6d$ and $7d$ elements. For the $6d$ elements the calculated removal energy is also given for one $7s$ electron, which is in the outermost shell (85)

periodic table to obtain the magnitude for 104 and then assumes that the increase along the $6d$ series as a function of Z will roughly parallel the $3d$ and $5d$ series. *Fricke and Waber* (85) and *Penneman and Mann* (89) have shown that Cunningham's values will be too low by about 10%, which leads to very high values at the end of the series, but also indicates that their chemical behavior is tending toward that of inactive noble metals with small maximal oxidation states.

Penneman and *Mann* (89) used Jørgensen's equations (8) and (9) with a k of 4.5 eV to predict the most stable states of elements 104–110 in aqueous solution. Jørgensen's selection of k applies to the hydrated cation (72, 73) and is not intended to account for the effects of complex ion formation or pH. The graph and tables of *Penneman* and *Mann* (89) yield the following most stable states in aqueous solution: 104(+4); 105(+5); 106(+4); (107+3); 108(+4); 109(+1); 110(0). In some cases, such as the +3 and +4 states of 108, the energies suggest they may be essentially as stable as the one listed.

Cunningham (88), using extrapolation, against the row of the periodic table, assumes that the pattern seen in oxidation states on going from the $3d$ to the $5d$ elements will continue into the $6d$. He obtains for the stable oxides: 104(+4); 105(+5); 106(+6); 107(+7); 108(+8); 109(+6); 110(+6). These results start deviating from those of *Penneman* and *Mann* at element 106. If solution conditions appropriate to the formation of oxyanions are established, oxidation states higher than those given by *Penneman* and *Mann* for 106, 107 and 108 would no doubt be attained, since the higher oxidation states of W, Re and Os are stabilized in this way. Such conditions would be closer to those assumed by *Cunningham*.

Radii for the $6d$ transition elements are given by *Fricke* and *Waber* (85). Their atomic and ionic radii were obtained using the principal maxima of the outermost electrons from DFS calculations. The metallic radii were obtained by complicated extrapolations of comparisons of the experimental trends as well as of the calculated trends of the radii of the outermost s and d electrons, taking into account empirically the fact that the outer electrons become more or less itinerant conduction electrons and are distributed over the crystal.

Penneman and *Mann* (89) also give an estimate of the metallic radii of the $6d$ elements, using for guidance the change in the calculated atomic radii of the $5d$ elements relative to the $6d$ elements as well as the experimental values. Their results are about 0.15 Å smaller than those of *Fricke* and *Waber*, involving a strong increase in density. Both estimates are listed in Table 3. One should bear in mind that both estimates are very rough extrapolations and can be used only as a first approximation. Estimates of the properties of the first four $6d$ elements were also given by *Häussinski* (90).

In the following we discuss each of the elements 104 to 112 separately. A list of their predicted properties is given in Table 3, the main references being (85, 88–92).

Element 104. (eka-hafnium) is predicted to resemble its homolog hafnium (element 72) in its chemical properties. It is expected to be predominantly tetrapositive, both in aqueous solution and in its solid compounds, although it should exhibit solid halides and perhaps aqueous ions of the +2 and +3 oxidation state as well.

One probably can predict some of the crystallographic properties, of the tetrapositive element 104 by extrapolation from those of its homologs zirconium and hafnium. The ionic radii of tetrapositive zirconium (0.74 Å) and hafnium (0.75 Å) suggest an ionic radius of about 0.78 Å for tetrapositive element 104, allowing for the smaller actinide rather than lanthanide contraction. Further one would expect the hydrolytic properties of element 104 and the solubilities of its compounds (such as the fluoride) to be similar to those of hafnium. The sum of

the ionization potentials for the first four electrons should be less than that for hafnium, which suggests that it should be easier to oxidize element 104 to the $+4$ ionic state although, of course, the formation of the $+4$ state in covalent form will not require the complete removal of all four electrons.

Element 105. (eka-tantalum) should resemble tantalum and niobium, with the pentavalent state being the most important. It should exhibit several oxidation states, such as $+4$ and $+3$, in addition to the more stable $+5$ state. There should be an extensive range of complex ions, offering a rich chemistry.

Element 106. The chemical properties of element 106 (eka-tungsten) are predicted to be similar to those of tungsten, molybdenum and to some extent chromium, offering an even richer chemistry of complex ions than these elements. The hexafluoride should be quite volatile and the hexachloride, pentachloride and oxychloride should be moderately volatile. Penneman and Mann predict a $+4$ oxidation state in aqueous solution. Jørgensen's selection of k is for the hydrated cation and is not intended to account for the effects of complex ion formation. However, since tungsten is stabilized in the oxidation state of $+6$ by the tungstate ion, an analogous situation may be expected for element 106.

Elements 107 and 108. Element 107 should be an eka-rhenium (with a volatile hexafluoride) and element 108 an eka-osmium, which suggests that the latter should have a volatile tetraoxide that would be useful in designing experiments for its chemical identification.

The differences in predictions of ionization states are large. The simple extrapolation of Cunningham suggests $+7$ and $+8$, whereas Penneman and Mann give $+3$ or $+2$ as the most stable state in aqueous solution. *Fricke* and *Waber* (67) predict $+5$ or $+6$. These inconsistent predictions may be taken as an indication that all of these oxidation states may exist, as is clear from the many possible oxidation states of the homologs Re and Os. Differences are expected in these elements, however, because of possible larger ligand field effects due to the greater spatial extension of the $6d$ orbital charge cloud, as stated by *Cunningham* (88).

Elements 109 and 110. The same arguments are expected to apply to elements 109 (eka-iridium) and element 110 (eka-platinum) but in much clearer fashion. The ionization energies will be much increased and the metals are expected to have an even nobler character. If the higher oxidation states $+6$ and $+8$, as predicted by *Cunningham*, are stable volatile hexa- and possibly octafluorides will form, which may be useful for chemical separation purposes. As with elements 107 and 108, this is contradicted by *Penneman* and *Mann* (89), who arrive at $+1$ and 0 as the most stable oxidation states in aqueous solution, and *Fricke* and *Waber* (67), who give $+3$ or $+2$ as the dominant oxidation states. Again, nearly all these states are expected in the actual chemistry of these elements. The prediction of the possible oxidation state 0 means that it might well be that these elements at the end of the $6d$ transition elements will remain as neutral atoms in the chemical separation processes, so that this method might fail. *Averill* and *Waber* (62) used the molecular orbital approach to estimate the stability of the hexafluoride of element 110. Their results indicate that this should be approximately as stable as the well-known platinum hexafluoride. Elements 109 and 110 should both have a strong tendency toward the formation of complex ions in their chemistry.

Table 3. Summary of predictions for elements 104 to 112

Element	104	105	106	107	108	109	110	111	112
Chemical group	IVB	VB	VIB	VII B	VIII	VIII	VIII	IB	IIB
Stable oxidation states ^{a)}	<u>4</u> , <u>3</u>	<u>5</u> , 4, 3	6, <u>4</u>	<u>5</u> , 7, <u>3</u>	<u>3</u> , <u>4</u> , 6, 8	3, 6, <u>1</u>	4, 2, 6, <u>0</u>	3	2
First ionization energy (eV) calc. (DF) ^{b)}	5.1	6.6	7.6	6.9	7.8	8.7	9.6	10.5	11.4
best expec. value				5.9	6.9	8.3	9.9	10.7	11.4
Second IP (eV) (DFS) extr.				18.7	17.6	18.9	19.6	21.5	21.1
Third IP (eV) (DFS) extr.				27.9	29.2	30.1	31.4	31.9	32.8
Fourth IP (eV) (DFS) extr.				37	38	40	41	42	44
Fifth IP (eV) (DFS) extr.				49	52	51	53	55	57
Atomic radius (Å) ^{d)}	1.49	1.42	1.36	1.31	1.26	1.22	1.18	1.14 1.2	1.10
Ionic radius (Å) ^{d)}	(+4) 0.71 0.78	(+5) 0.68	(+4) 0.86	(+5) 0.83	(+4) 0.80	(+3) 0.83	(+2) 0.80	(+3) 0.76	
Metallic radius (Å) ^{e)}	1.66	1.53	1.47	1.45	1.43	1.44	1.46	1.52	1.60
^{e)}	1.50	1.39	1.32	1.28	1.26	1.28	1.32	1.38	1.47
Density (g/cm ³) ^{e)}	17	21.6	23.2	27.2	28.6	28.2	27.4	24.4	16.8
^{e)}	23.2	29.3	35.0	37.1	40.7	37.4	34.8	28.7	23.7
Heat of sublimation (kcal/mol)				220	201	180	210	125	small
Standard electrode potential (V) ^{f)}	0 → +4 < 1.7								
Melting point (°C) ^{f)}	2100						Electron affinity (eV) ~ 1.6		
Boiling point (°C) ^{f)}	5500								

^{a)} The underlined values are the oxidation states in aqueous solution as given in Ref. (89). ^{b)} Ref. (35). ^{c)} Unpublished. ^{d)} Ref. (67).
^{e)} Ref. (56). ^{f)} Ref. (26) in Ref. (85). ^{g)} Ref. (93).

Element 111. (eka-gold) has been studied in great detail by *Keller, Nestor, Carlson and Fricke (93)*. They used valence-bond theory to predict the most stable oxidation state $+3$ of this element. In $\text{Au}(+3)$ compounds the ligands form a square-planar arrangement around the central Au ion, indicating ds^2 hybridization of its orbitals. The $5d$, $6s$, and $6p$ electrons are used for bonding and another pair of electrons is accepted from an anion to form complexes such as AuCl_4^- . The promotion energy from the $6d^{10}6s^1$ ground state to the $5d^96s^16p^1$ is about 5.9 eV compared with 6.2 eV for the promotion from the $6d^97s^2$ ground state in element 111 to the analogous hybridized configuration. Because the atomic radius of 111 will be 1.2 Å, whereas that of gold is 1.35 Å, element 111 should form at least as strong bonds as Au since the hybridization orbitals are not diffused over as large a volume. Also, the heats of sublimation of 111 and Au should be very similar because the breaking of the full d shell will be nearly compensated for by the filled s shell. The smaller atomic radius of 111 and its higher ionization potential suggest further that the heat of sublimation may be slightly higher rather than slightly lower.

These energy-expending processes, the heat of sublimation and the promotion to the $+3$ state, will be more than compensated for by the energy released in bond formation because the smaller radius of 111 will allow larger orbital overlap with ligand orbitals. *Keller et al.* therefore expect 111 to be stable in the oxidation state $+3$ and to have a chemistry similar to $\text{Au}(+3)$. The $+1$ state of element 111 will be very unstable and, if it exists at all, it will be in complexes with strongly polarizable ligands such as cyanide. $111(+2)$ is not expected to exist. An interesting feature will be the possible stability of the 111^- ion, analogous to the auride ion. The expected electron affinity of element 111 lies between that of Au, which forms the negative auride ion in chemical compounds like CsAu and RbAu , and Cu and Ag which do not.

Element 112. Similar detailed considerations concerning the chemical properties have not yet been made (85, 91, 94) for element 112 (eka-mercury). More qualitative conjectures suggest that the most stable oxidation states will be the $(+1)$ and $(+2)$ states, but that higher oxidation states will probably be important in aqueous solution and in compounds. In macroscopic quantities it should be a distinctly noble metal, but because both the $6d$ and $7s$ outer electron shells are filled and their ionization energies are higher than in all the homologs, one may argue that the interatomic attraction in the metallic state will be small, possibly even leading to high volatility as in the noble gases. Element 112 should have an extensive complex ion chemistry, like all the elements in the second half of the $6d$ transition series. A general feature of these elements is the expected marked tendency to be "soft" acceptor ions. In Fig. 13, in which the logarithm of the stability constant for the halide compounds is plotted for the subgroup-IIB elements, a marked increasing softness for the higher elements can be seen. *Kratz* and co-workers (94) concluded from this figure that 112^{+2} should form very stable iodine and bromine complex ions, which would be extremely useful for the chemical separation. However it is also possible that this element might show a very low chemical activity and simply remain in its neutral atom configuration.

In Table 3 the predicted properties of the $6d$ -transition elements are briefly summarized.

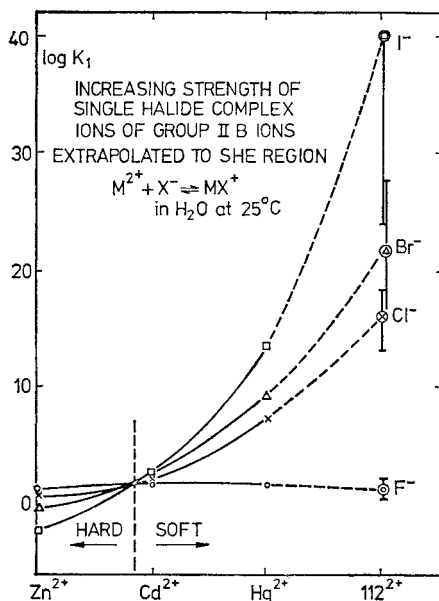


Fig. 13. Logarithm of the stability constant for the halide compounds of the group-II B elements (94)

2. The $7p$ and $8s$ Elements $Z = 113$ to 120

The lifetimes of the elements near $Z = 114$ are expected to be years or even longer. Hence a knowledge of their chemical behavior is most important, since it might even be possible to find small amounts of those elements on earth, although the experimental sensitivity of these searches has reached 10^{-14} g/g with no clear evidence of the existence of superheavy elements (32).

As can be seen from the Hartree Fock calculations in Table 2, from elements 113 to 118 the $7p$ electrons will be filled in, elements 119 and 120 following with the $8s$ electrons. The energy eigenvalues from DFS calculations (85) of the outer electrons of these elements are compared with the analogous values for the $6p$ elements Tl to Ra in Fig. 14. The great similarity in the occupation pattern of the valence electrons is evident. However, there are two significant differences. The analogous s electrons are bound more tightly for higher Z ; this binding results from the large direct relativistic effects, as discussed in Section III.2a. The spin-orbit splitting of the $7p$ shell has increased compared to the $6p$ shell. A complete subshell with quantum numbers $|nlj\rangle$ is spherically symmetric, just as the complete nonrelativistic $|nl\rangle$ shells are, which means that there will be a change in the angular distribution of the electrons in the relativistic treatment, which could lead to differences in chemical behavior for incomplete $|nlj\rangle$ subshells of very heavy elements. The first ionization potentials of the p elements can be seen in Fig. 15, where the experimental ionization energies for the 3rd, 5th and 6th periods are shown together with the calculated values for the 6th, 7th and

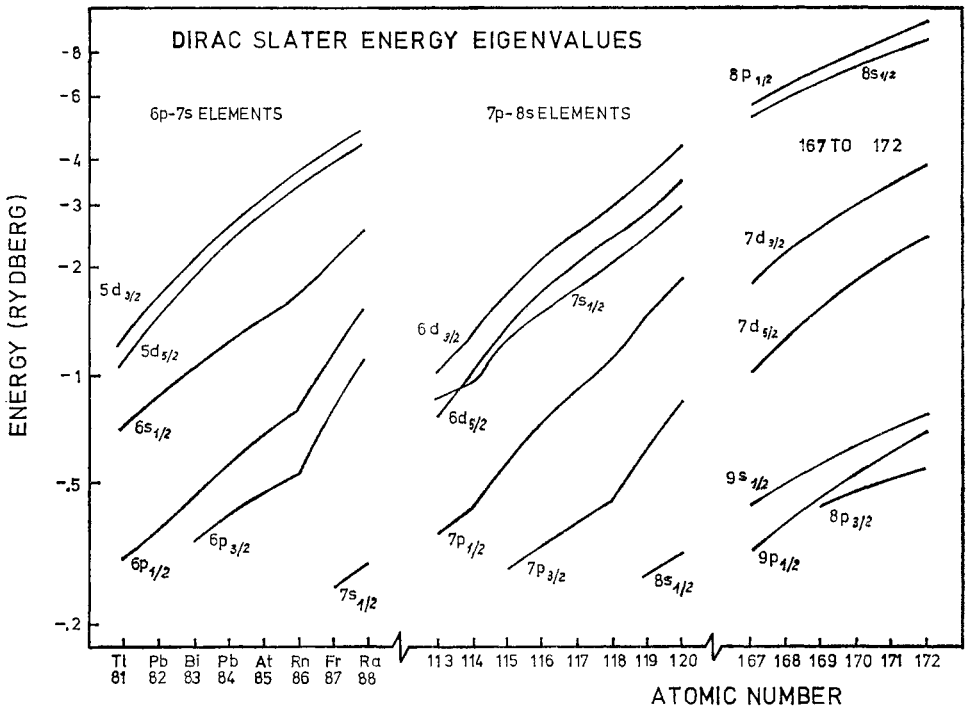


Fig. 14. Dirac-Slater (DFS) energy eigenvalues of the outer electrons for the $6p$ – $7s$ and $7p$ – $8s$ elements as well as for elements 167 to 172. This figure demonstrates the strong increase of the splitting of the p subshells. For elements 167 to 172, the $9p_{1/2}$ and the $8p_{3/2}$ subshells are energetically so close to each other that they form a p shell which is comparable to the $3p$ shell (85)

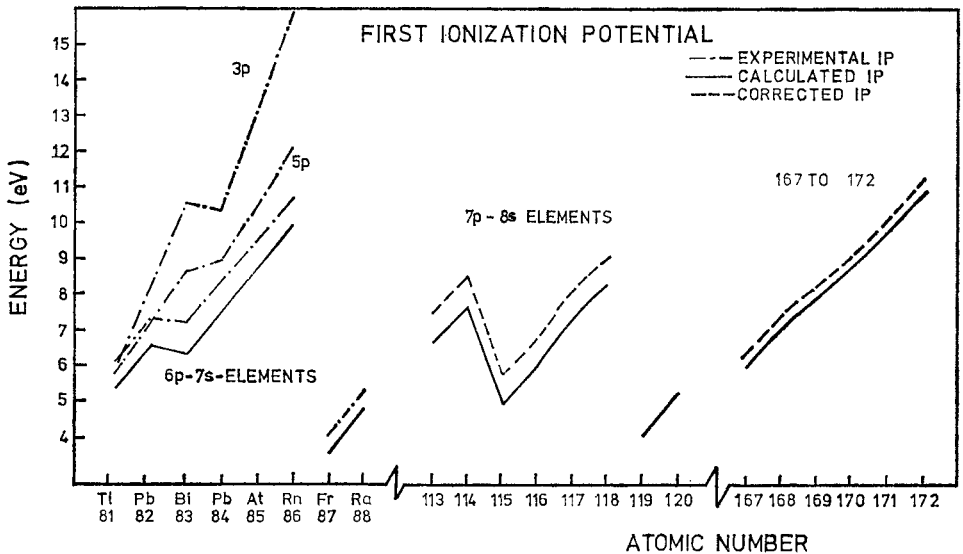


Fig. 15. First ionization energies for the $6p$ – $7s$ and $7p$ – $8s$ elements as well as elements 167 to 172. For comparison, first ionization energies for the $3p$ and $5p$ elements are also given (85)

9th periods. This figure is located below Fig. 14 to assist comparison of the trends of the energy eigenvalues and ionization energies. The ionization energy in the early periods increases linearly with only one break between configurations p^3 and p^4 . This behavior is caused by the half-filled shell where three electrons occupy the three possible p orbitals with parallel spin. The pairing energy is negative so that the ionization energy is smaller for the 4th electron. This effect of the Russell-Saunders coupling is very significant in the first periods but becomes smaller for the higher periods, because the LS coupling changes to intermediate coupling and from there to $j-j$ or spin-orbit coupling. In the 6th period, the break between p^3 and p^4 has vanished but instead a break occurs between p^2 and p^3 ; this trend is expected, since the spin-orbit coupling becomes more important than pairing energy in the $p_{1/2}$ and $p_{3/2}$ subshells. This break becomes even larger for elements 113 to 118. Thus, the ionization energy of element 114 is nearly as large as the same value for the "noble gas" that occurs at $Z = 118$. The experimental and calculated curves for the 6th period are almost parallel with a difference of about 0.8 eV. Therefore, the first ionization energies of elements 113 to 118 have been enlarged by 0.8 eV to get more realistic values (56). The estimated error is expected to be about $+0.4$ eV. Of course, it is even better to extrapolate these differences for every chemical group separately, as is done in detailed discussion of the elements (78).

The oxidation states of elements 113 to 118 are expected to follow the systematic trends for group-III to VIII elements, that is, elements with higher Z prefer the lower oxidation states. In the first part of the p elements this is the expression of the fact that the s electrons with their greater binding energy lose their chemical activity as Z increases, so that the p electrons will be the only valence electrons available; in the second part the same holds true for the $7p_{1/2}$ electrons, which form a spherical closed shell (at least in $j-j$ coupling), so that only the $7p_{3/2}$ electrons will remain chemically active.

In predicting the atomic and ionic radii of these elements, one gets into difficulties. The concept of atomic radii of Slater (63), who says that the atomic radius can be well defined as being the radius of the principal maximum of the outermost electron shell, *i. e.* of the frontier orbital, works quite well in most parts of the periodic system. However, at the end of the d transition elements and for most of the p elements, this definition apparently yields inaccurate results. The reason for this behavior is not quite clear but it may be connected with the type of bonding, *i. e.* the large hybridization effects in the compounds of these elements. Therefore a continuation of the trends of the behavior of the metallic or ionic radii, as done by Grosse (95), Keller *et al.* (78), and Cunningham (96), is expected to give more accurate results. Fricke and Waber (56) predicted the metallic radii of these elements on the basis of a comparison of the computed total electron density at large radii of known elements. The metallic radius of the superheavy elements was assumed to be where the density was equal to the density of the known analogous elements at its experimental radius.

Several compounds of elements 112 to 117 have been studied theoretically in great detail by Hoffmann and Bächmann (75, 76) as well as by Eichler (77), because the gaseous hydrides, chloride and a few other compounds, may be used for quick chemical separation by the method of gas chromatography. We do not list

their straight extrapolations in the tables because it would be necessary to give for every compound the values of boiling point, heat of sublimation, heat of vaporization, enthalpy, heat of formation, dissociation energy, ionization potential, etc. For these values, we therefore refer to the literature.

Element 113. Detailed predictions of element 113 (eka thallium) have been given by *Keller et al.* (78). In this chemical group IIIA the main oxidation state is 3; only Tl has also a monovalent state which is associated with the ionization of the single $6p_{1/2}$ electron and the relatively increased stability of the $6s$ electrons. From this behavior, the high ionization energy of the $7p_{1/2}$ electron, and the even more increased stability of the $7s$ electrons, the principal oxidation state of element 113 is expected to be +1.

The straightforward extrapolations of *Keller et al.* of the physical and chemical properties of elements 113 and 114 are mainly based on the fact of the simple outer electronic structure of $7p_{1/2}$ and $7p_{1/2}^2$, with their large energetic and radial separation to the $7s$ and $6d$ electrons. As an example of these predictions, which are listed in Table 5, Fig. 16 shows the very suggestive extrapolations of the heat of sublimation of elements 113 and 114, and Fig. 17 the extrapolation of the melting point of element 113. The second important quantity for the derivation of the standard electrode potential through the Born Haber cycle is the ionization

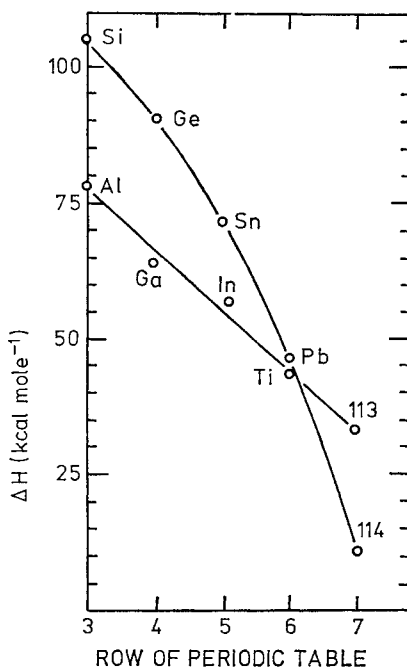


Fig. 16. The evaluation of the heat of vaporization for elements 113 and 114 is shown as an example of the extrapolation of chemical and physical properties, as performed by *Keller et al.* (78)

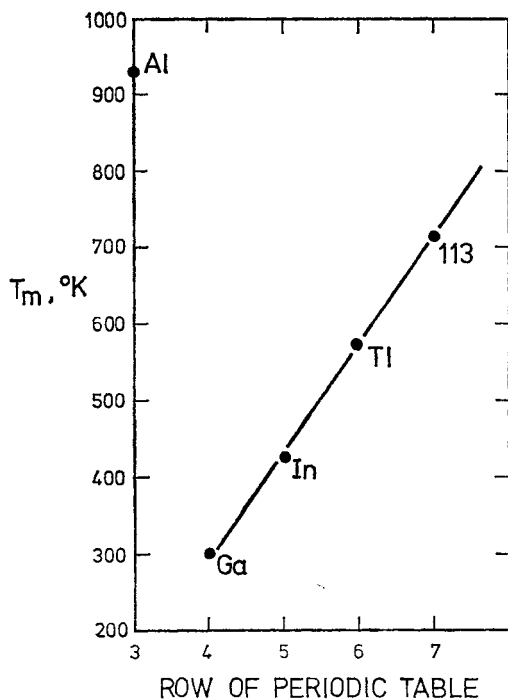


Fig. 17. Extrapolation of the melting point of element 113 (78)

potential. In Table 4 we show the method used to derive this quantity by means of both calculation and extrapolation. The value in parentheses is expected to be the best value. The third quantity needed is the single-ion hydration energy, $H_M^n +$. *David* (74) obtained $75 \text{ kcal (g atom)}^{-1}$ for $H_{113} +$ whereas *Keller* (78) preferred to use the Born equation and obtained $72 \text{ kcal (g atom)}^{-1}$. These values lead to a

Table 4. Example of the extrapolation of calculated and experimental ionization energies to the best values for element 113. The calculated values are taken from DFS calculations (78)

Element	First Ionization Potential (eV) (Group III A)		
	calculated	experimental	Δ
Al	4.89	5.98	1.09
Ga	4.99	6.00	1.01
In	4.87	5.78	0.91
Tl	5.24	6.11	0.87
113	6.53	(7.36)	(0.83)

standard electron potential of +0.6 volts for element 113, which indicates that element 113 will be somewhat less active than Tl.

To summarize the chemistry which can actually be expected for element 113, one may say that it is in general expected to fall between that of Tl^+ and Ag^+ . 113^+ is expected to bind anions more readily than Tl^+ so that $(113)Cl$ will be rather soluble in excess HCl whereas the solubility of $TlCl$ is essentially unchanged. Similarly, $(113)Cl$ is expected to be soluble in ammonia water in contrast to the behavior of $TlCl$. The behavior of the 113^+ ion should tend toward Ag^+ in these respects. Also, although $Tl(OH)$ is soluble and a strong base, the 113^+ ion should form a slightly soluble oxide that is soluble in aqueous ammonia.

Element 114. (eka-lead) is of special interest because of its expected double-magic nucleus with a possible long lifetime. It belongs to the group-IV elements (78) where the stability of the oxidation state +4 decreases and +2 increases with increasing Z . The tetravalency in this chemical group IV is connected with a sp^3 hybridization and strong covalent bonding. The energetic difference between the ns and the average of the np electrons increases for the higher periods, as can be seen in Fig. 7, as the result of the relativistic effects. Also, the spin of the p electrons couples strongly to their own angular momentum. Therefore, a sp^3 hybridization is no longer easily possible for 114, which means that the predominant oxidation state of 114 will be divalent. However, since the outermost s and d electrons in 114 have approximately equal energies, some form of sd hybrid would be possible. Thus, one cannot exclude the possibility that a volatile hexafluoride might form. Because the $7p_{1/2}^2$ shell, in 114 approximates to a closed shell analogous to an s^2 closed shell such as is found in mercury, it is worthwhile comparing what one finds on going from 113 to 114 with what is known about going from Au (with a s^1 configuration) to Hg (with a s^2 configuration) in addition to the chemical group extrapolations. The results are given in Table 5. The standard electrode potential derived from these values by *Keller et al.* for element 114 is +0.9 volt, so that it is expected to be more noble than lead. If the error of ± 1.0 volt is negative, the value would be about the same as lead. *Jørgensen* and *Haissinsky* (97) suggest that 114 may even be alkaline earth-like in its chemistry, which seems to be extremely far away from *Keller's* (78) results.

Summarizing, one can say due to relativistic effects the +2 valency of element 114 is strongly favored and is expected to resemble Pb^{+2} chemistry, with a still greater tendency to form complexes in solution. In excess halogen acid, complexes of the type $114 X_n^{(n-2)}$ should be stable. A complex analogous to the plumbite ion is expected. The sulfate and sulfide should be extremely insoluble, but the acetate and nitrate soluble. The latter may show extensive hydrolysis. *Hofmann* (98) discusses the probable presence of element 114 in nature as a result of its chemical behavior.

Element 115. A most intriguing situation is offered by element 115 (eka-bismuth) because a $7p_{3/2}$ electron is added here outside the $7p_{1/2}^2$ closed shell. As pointed out by *Fricke* and *Waber* (85), the $7p_{3/2}$ binding energy is much less than that of the $7p_{1/2}$ electrons. Consequently, they predict that element 115 will have +1 as its normal oxidation state. *Keller*, *Fricke* and *Nestor* (99) have recently obtained preliminary results indicating that the +1 state will act like Tl^+ . This prediction is based on the values they have obtained for the ionization energy,

Table 5. Summary of predictions for elements 113 to 120

Element	113 ^{e)}	114 ^{e)}	115 ^{f)}	116	117 ^{g)}	118 ^{g)}	119 ^{g)}	120 ^{g)}
Chemical group	IIIA	IVA	VA	VIA	halogen	noble gas	alkali	alkaline earth
Stable oxidation states	1,3	2	1,3	2,4	3,1,5,-1	4,2,6	1, others	2, others
Ionization potentials (eV)								
I best value	7.4	8.5	5.5	7.5				
I DF calculation ^{a)}	8.0	8.9	5.5	6.6	7.7	8.7	4.8	6.0
II (DFS)	23.2	16.6	18.2	13.8		16.2	17.6	
III (DFS)	33.2	34.9	27.5	29.5				
IV (DFS)	45.1	45.6	48.5	39.5				
V (DFS)	59	60.6	59.3	63				
Standard electrode potential (eV)	(0 → 1) +0.6	(0 → 2) +0.9	(0 → 1) +1.5		(-1 → 0) +0.25 -0.5		(0 → 1) 2.9	(0 → 2) 2.9
Atomic radius (Å)			2.0				2.4 ^{h)}	2.0 ^{h)}
Ionic radius (Å)	(+1) 1.4	(+2) 1.2	(+1) 1.5 (+3) 1.0				(+1) 1.8	(+2) 1.6
Metallic radius (Å) ^{b,c)}	1.7 1.62	1.8 1.68	1.87 1.67	1.83 1.69			2.4	2.0
Density (g/cm ³)	16	14	13.5	12.9			3 ^{k)}	7 ^{k)}
Melting point (°C)	430	67	400		350-550	-15	0-30	680
Boiling point (°C)	1130	147 ^{e)} ~ 1000 ^{l)} 2840 ^{m)}			610	-10	630	1700
Heat of vaporization (kcal/g-atom)	31	9	33	10				
Heat of sublimation (kcal/g-atom)	34	10	34	47			10	33
Standard enthalpie (kcal/g-atom) ^{d)}	26 ± 2	17 ± 4	36 ± 3	20 ± 4	19 ± 2			
Entropy (cal deg ⁻¹ (g-atom) ⁻¹)	17	20	16					

a) Ref. (35). b) Ref. (56). c) Ref. (89). d) Ref. (77). e) Ref. (78). f) Ref. (99).

g) The properties below the ionization potentials are from *B. B. Cunningham* to be found in Ref. (5).

h) Ref. (85). k) Ref. (91). l) Ref. (98). m) Ref. (108).

ionic radius, and polarizability, which show that 115^+ is much more similar to Tl^+ than to Bi^+ . An oxidation potential of 1.5 volts is predicted, indicating that the 115 metal is quite reactive.

The chemistry of the 115^+ ion can be summarized as follows: the complexing ability of 115^+ can be expected to be low with such anions as the halides, cyanide and ammonia. Hydrolysis should occur readily for 115 in the oxidation state of 1, and the hydroxide, carbonate, oxalate and fluoride should be soluble. The sulfide should be insoluble and the chloride, bromide, iodine, and thiocyanide only slightly soluble. For example, excess HCl will not appreciably affect the solubility of $(115)Cl$.

Smith and Davis (100) have recently discussed Bi^+ chemistry in the hope that this may give some insights into 115^+ chemistry. *Keller, Fricke and Nestor (99)* have also obtained a preliminary estimate of the stability of $115(+3)$ by analogy to $Tl(+3)$. In their treatment they regard the $7p_{1/2}^2 7p_{3/2}$ valence state of $115(+3)$ to be analogous to the $6p6s^2$ valence state of $Tl(+3)$. Consideration of the promotion energy and heat of sublimation of 115 relative to those of Tl, plus the expected overlap of its orbitals with those of ligands, lead to the conclusion that the oxidation state of +3 will be quite important in 115 chemistry besides the +1 state. But, as in the arguments used for the +1, state the 115^{+3} ion is expected to be most like Bi^{+3} . The trichloride, tribromide, and triiodide of 115^{+3} will probably be soluble, and they may show a tendency to hydrolyze to form salts analogous to $BiOCl$ and $BiOBr$. The trifluoride should be insoluble like BiF_3 as well as $(115)S_3$. The sulfate and nitrate will be soluble in the appropriate acids, and the phosphate will be insoluble.

It is not yet possible to predict the relative stabilities of the +1 and +3 states. In fact, their relative stabilities may well depend strongly on the state of complexation or hydrolytic conditions. On the other hand, element 115 will not show the group oxidation state of +5. The other properties of the element may be found in Table 5.

Because element 114 behaves to some extent like a closed-shell atom, and element 115 as if a new group of elements had been started, we give in Fig. 18 the results of *Eichler (77)* from the extrapolation of the standard enthalpy of elements 112 to 117. The relatively small value for 114 and the relatively large value for 115 may be taken as another indication that the interpretation given here, arising from the atomic calculations with the relativistic effects, will be important as regards many physical quantities as well as in the chemical interpretation of these elements.

Element 116. Not much work has been done on element 116 (eka-polonium) beside the normal extrapolations and calculations of the ground state and ionized configurations (85). The values obtained are listed in Table 5. The chemical properties of element 116 should be determined by extrapolation from polonium; thus it should be most stable in the +2 state with a less stable +4 state.

Element 117. (eka-astatine) is expected to have little similarity to what one usually calls a halogen, mainly because its electron affinity will be very small. *Cunningham (96)* predicted its value as 2.6 eV, whereas the calculations of *Waber, Cromer and Liberman (54)* gave a value of only 1.8 eV. As a result of this small electron affinity, and from extrapolations of the chemical properties of the

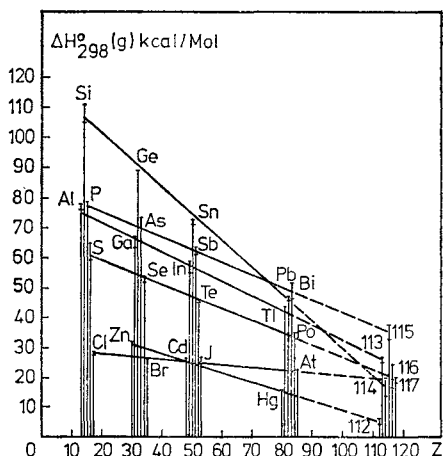


Fig. 18. Extrapolation of the standard enthalpy for elements 112 to 117, as given by *Eichler* (77)

lighter halogen homologs, all authors agree that the +3 oxidation state should be at least as important as the -1 state, and possibly more so. To take an example, element 117 might resemble Au(+3) in its ion-exchange behavior with halide media. *Cunningham* (96) describes the solid element 117 as having a semi-metallic appearance.

Element 118. *A. V. Grosse* wrote a prophetic article (95) in 1965 before the nuclear theorists began to publish their findings concerning the island of stability. In this paper he gave detailed predictions of the physical and chemical properties of element 118 (eka-radon), the next rare gas. He pointed out that eka-radon would be the most electropositive of the rare gases. In addition to the oxides and fluorides shown by Kr and Xe, he predicted that 118 would be likely to form a noble gas-chlorine bond. These very first extrapolations into the region of super-heavy elements have been fully confirmed by the calculations, because the first ionization potentials turn out to be much lower than in all the other noble gases.

Independently *Grosse* (95) and *Cunningham* (96) found that the expected boiling point of liquid element 118 is about -15°C , so that it will be nearly a "noble fluid". Because of its large atomic number it will, of course, be much denser than all the other noble gases. But, in general, the chemical behavior of element 118 will be more like that of a normal element, with many possible oxidation states like +2 and +4; +6 will be less important because of the strong binding of the $p_{1/2}$ electrons. It will continue the trend towards chemical reactivity first observed in xenon.

Elements 119 and 120. In the two elements 119 (eka-francium) and element 120 (eka-radium) the 8s electrons will be bound very tightly and therefore these two elements are expected to be chemically very similar to Cs and Ba or Fr and Ra. Fig. 14 shows the energy eigenvalues of the outer electrons and Fig. 15 the ionization potential for elements 119 and 120 drawn in comparison to Fr and Ra. The main oxidation state of 119 and 120 will be 1 and 2, as is normal for alkali and

alkaline earth metals. Their ionization potential will be about 0.5 eV higher than in the elements Fr and Ra, mainly because the s electrons penetrate deep into the atom and feel the very strong potential near the nucleus. Therefore, their atomic radius according to the simple definition of *Slater (63)* is expected to be 2.4 and 2.0 Å, very similar to the values for Rb and Sr. This decreasing trend in the radius can best be seen in Fig. 10. The same holds true for the ionization energy displayed in Fig. 15. Therefore the early predictions of *Cunningham (96)*, who extrapolated the trends of the known alkali and alkaline earth elements, have had to be corrected so that the chemistry of elements 119 and 120 will be closer to Rb and Sr than to Fr and Ra in the +1 or +2 oxidation states, respectively. On the other hand, the ions will have larger radii than Rb^+ and Sr^{2+} because of the larger extension of the filled $7p$ shell in comparison to the lower p shells, so that hydration will be more important and crystal energies will be different. Another important point is that higher oxidation states may be reached (85) in the presence of strong oxidizing agents because the ionization energy of the outer $7p_{3/2}$ electrons is only of the order of 10 eV. *Penneman and Mann (89)* came to the same conclusion; thus, an oxidation state of +3 and +4 should be considered.

Table 5 gives the chemical and physical properties of elements 119 and 120.

3. The $5g$ and $6f$ Elements $Z = 121$ to 154

The next elements of the periodic table, starting with element 121; belong to a very long, unprecedented transition series which is characterized by the filling of not only the $6f$ but also the $5g$ electrons. *Seaborg (5)* called these elements *Superactinides*.

Unfortunately, it is expected that the chemistry of these elements will not be able to be studied because the theoretical investigations of nuclear stability predict that these elements will be unstable and have very short lifetimes. Before this was known, a large number of theoretical calculations of the ground-state electronic configurations were made in this region because the proton number $Z = 126$ was long expected to be the center of the first island of stability. Now this is considered unlikely. Nevertheless, the chemistry of these elements would be very interesting.

In the lanthanoides and actinoides, the competition between the outer d and inner f electrons determines the ground-state electron configuration as well as the chemistry of these elements. Here at the beginning of the superactinides, not merely two but four electron shells, namely the $8p_{1/2}$, $7d_{3/2}$, $6f_{5/2}$ and $5g_{7/2}$, are expected to compete nearly simultaneously in the atom, and these open shells together with the $8s$ electrons determine the chemistry. The results of the ground-state calculations of these elements can be found in Table 2.

Three most interesting things occur in elements 121 to 154. First, the $8p_{1/2}$ electrons are filled, beginning with element 121, and at least one of these electrons remains in all following elements. This is clearly a direct relativistic effect, which is most effective for all $j = 1/2$ levels. Second, during the filling of all the superactinide elements some other electrons besides the $5g$ and $6f$ electrons always remain in the ground-state configuration in contrast to the analogous lanthanoides and actinoides, where at the beginning some d electron states are occupied but are

removed during the filling of the f shell. Third, the effective binding of an electron with large values of the angular momentum is accompanied by the radial collapse of the orbital, the centrifugal term $l(l+1)/r^2$ keeping it extended. For example, the effective radius of the $5g$ electrons changes from 25 Bohr units in element 120 in the excited configuration $8s^15g^1$ to 0.8 for element 121 in the configuration $8s^17d^15g^1$, according to *Griffin et al. (101)*, as shown in Fig. 19. This demonstrates that large changes occur in this case, although the change in the effective potential is relatively small. The best calculations which are from *Mann (35, 50)* show that this collapse actually occurs as late as element 125 as a consequence of the indirect relativistic effect.

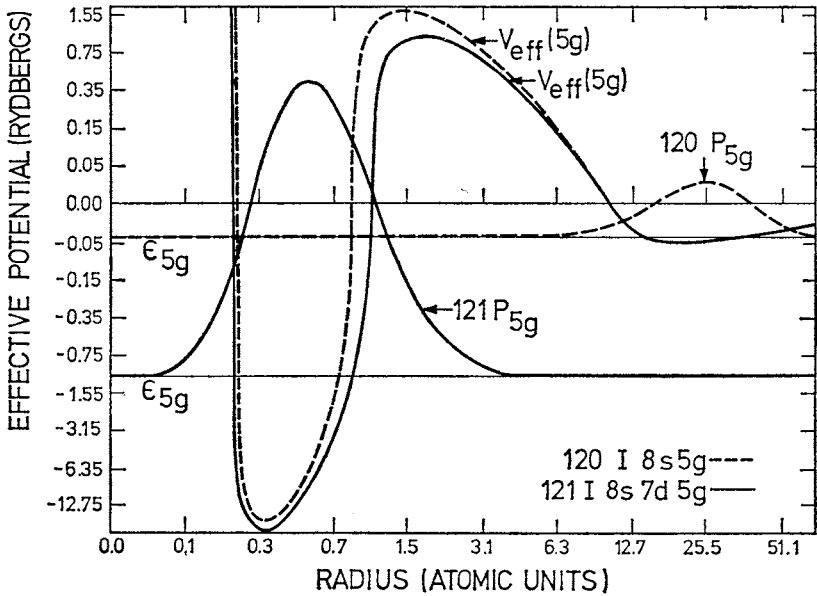


Fig. 19. Effective potentials for the $5g$ electron in element 120 with configuration $8s5g$ and element 121 with configuration $8s7d5g$. Although the change in the potential is relatively small, the $5g$ wave function changes its radius from 25 Bohr units to about 0.6 Bohr units (*101*)

The early onset of the $7p$ shell filling at element 121 can only be understood as a consequence of the large spin-orbit splitting. A discussion of the level structure of the first two elements of the superactinide series, 121 and 122, has been given by *Mann and Waber (50)* and *Cowan and Mann (102)*. We reproduce in Fig. 20 the level structure of element 121 in comparison to its homolog actinium. The solid lines represent subconfigurations for the individual sets of quantum numbers $|nlj\rangle$ and the barycenter, which is the weighted average taken over the j values, is indicated by a dashed line. Figure 20 nicely shows the large effect of the spin-orbit splitting, which brings a $8p$ electron into the stable atomic ground-state of the first superactinides.

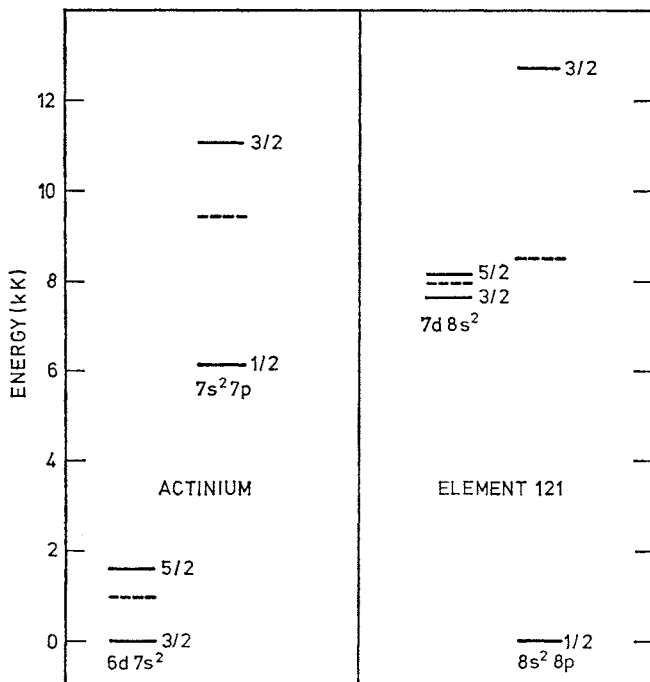


Fig. 20. Calculated term levels of the ds^2 and ps^2 configurations of actinium and element 121. The dashed lines indicate average energies (50)

The very small binding energies of all electrons in the $8s_{1/2}$, $8p_{1/2}$, $7d_{3/2}$, $6f_{5/2}$ and $5g_{7/2}$ shells makes it plausible that most of these electrons can be oxidized in chemical compounds so that very high oxidation states might be reached in complex compounds. This is in accordance with the trend observed among the lanthanoides, where practically only one oxidation state of 3 is possible, to the actinoides with high oxidation states at the beginning and small oxidation states at the end. Hybridizations of unknown complex character will be possible because the four shells are far enough extended radially and are thus available for hybridization with different angular momenta but nearly the same energy.

With regard to the formation of ionic compounds, it is not too relevant whether the $8p$ or $7d$ shell is occupied in the neutral atom, as studied *in extenso* by Mann and Waber (50). Instead, the significant question for more ionic compounds is whether in the ions, after all outer s , p and d electrons are removed, some g or f electrons will be in frontier orbitals or whether they might be easily excited to an outer electron shell so that they can be removed as well. Prince and Waber (103) showed that even in the divalent state of element 126 one g electron has changed to an f electronic state. However, the $8s$ electrons are not the first to be removed. Thus, the divalent ions will be expected to act as soft Lewis acids and possibly form covalent complex ions readily. Crystal or ligand fields influence the nature of the hybridization. Details such as directionality of bonds

will be determined by the occupation of the frontier orbitals and, of course, by the approaching anion. Only a few calculations for highly ionized states have been done to date. However, from a comparison of the energy eigenvalues of the different shells, it seems that oxidation states may well reach very high values at about, or near element 128 in complex compounds, but that normally these elements will have 4 as their main oxidation state in ionic compounds.

The main reason for this expectation is the observation that the ionization energies increase dramatically with increasing ionization and are soon out of the chemical-energetic range. In addition, there is also a limit imposed by geometrical considerations. In an early paper, *Jørgensen* (104) concludes that element 126 will be mainly tetravalent. The maximal valency will be reduced to 6 at element 132 and in the region of 140 it will be three to four. At the end of the superactinide series, the normal oxidation states are expected to be only 2 because the $6f$ shell is buried deep inside the atom and the $8s$ and $8p_{1/2}$ electrons, which are in frontier orbitals, are bound so strongly that they will be chemically inactive (see Fig. 8); only the $7d$ electrons will be available for bonding. To be more specific, the calculations show that in elements around 156 the shell is nearly full and only two $7d$ electrons which extend radially beyond the $8s$ and $8p_{1/2}$ shell are available. This behavior seems very similar to that of the low oxidation states at the end of the actinoides.

The lanthanoid contraction of about 0.044 \AA per element is larger than the actinoid contraction of about 0.03 \AA per element, because the $4f$ wave function is less localized than the $5f$ wave function and shrinks more rapidly with increasing nuclear charge. The analogous contraction is expected in the superactinide series. The total effect will be very large because of the 32 electrons, which will be filled in the deep $5g$ and $6f$ shells. From a comparison of the outer-electron wave functions of the lanthanoides, actinoides and superactinides, a contraction of about 0.02 \AA per element can be expected, starting with element 121 and continuing to element 154. This can also be seen in Fig. 9.

As a conclusion regarding chemical predictions of these elements, one may say that predictions in this region is somewhat unreliable, first because most of these elements have no homologs; secondly, because we are already well into an unknown region; and third, because relativistic effects have a large influence on these elements. But it is possible to say from the calculations that chemical behavior will be very different for the elements at the beginning, where high oxidation states will readily be reached, and the end where, due to the strong binding of the outermost electrons, the chemical character will be very noble, so that very low oxidation states will be possible.

4. The Elements $Z = 155$ to 172 and $Z = 184$

Because there is still a faint possibility that some elements near the magic proton number 164 may have half-lives long enough to permit a chemical study, a discussion of these elements is not purely academic.

The results of the calculations by *Fricke* and *Waber* (56) and *Mann* (35), which are listed in Table 2, show that formally elements 155 to 164 are the d transition elements of the 8th period.

The relativistic enhancement of the subshells with $j = 1/2$ is so large that in the elements 165 to 168 the $9s$ and $9p_{1/2}$ states will be occupied instead of the $8p_{3/2}$ state. Hence the filling of the $8p_{3/2}$ electrons can occur only in elements 169 to 172. This surprising result makes it possible to give the formal continuation of the periodic table shown in Fig. 21, because there are six p electrons available from two different shells which are energetically very close, so that they will nicely form a "normal" p shell. Therefore, the 9th period will be quite analogous to the 2nd and 3rd periods in the periodic system. This continuation and the differences from the normal expected continuation are discussed below.

Elements 156 to 164. In the periods before the 8th period, normally all d and p elements are influenced in their chemical behavior more or less by the outer s electrons. This is no longer true for the d transition elements 155 to 164, where the $8s$ and $8p_{1/2}$ electrons are bound so strongly that they do not participate in the chemical bonding. Fig. 22 shows the outer electronic wave functions of element 164 with the deeply buried $8s$ and $8p_{1/2}$ electrons. This electronic structure is quite similar to that of the d elements of the lower periods, where the outer s electrons are removed. One might therefore argue that, as a first guess, the aqueous and ionic behavior of an E^{m+2} ion of the lower d elements is comparable to an E^m ion of elements 155 to 164 after making allowance for the different ionic sizes and charge. But because the $9s$ and $9p_{1/2}$ states are easily available in 164 for hybridization, the chemical behavior is expected not to be too different from that of the other d elements. *Penneman et al.* (71) gave a very extensive and sophisticated chemical discussion of element 164. They conclude that it would be chemically quite active. In aqueous solution it will be predominantly bivalent, but stronger ligands will form tetra- and hexavalent bonds. Although in its bivalent form it may be compared with lead, it is quite conceivable that tetrahedral $164(\text{CO})_4$ and $164(\text{PF}_3)_4$ and linear $164(\text{CN})_2^{-2}$ might be prepared, which would be in rather striking contrast to lead. They find element 164 to be a soft Lewis acid with an Ahrlands softness parameter close to 4 eV, which is very near to the value for mercury. This comparison with Hg agrees well with the position that *Fricke, Greiner and Waber* (56) have allocated this element in the periodic table shown in Fig. 21.

Penneman et al. (72) arrived at their chemical conclusions from calculations of very high ionization states and a number of semi-empirical formulas, partly discussed in Section III. 2b. They agree with *Fricke et al.* (85) that the metallic form might be quite stable, which again is a result of the deeply buried $8s$ and $8p_{1/2}$ electrons and the readily available $7d$ electrons. This metallic form should have a larger cohesive energy than almost any other element because of the covalent bonding, so that its melting point should be quite high. *Fricke et al.* (85) compare element 164 with element 118 for formal reasons, also. The structures of the valence electrons with a filled outer shell, the ionization energies, the radii, the energy eigenvalues, and the energetic splitting of the filled d states in element 164 and the p shell in element 118 are very similar. Therefore, if element 118, ever becomes available, a detailed experimental study, could also lead to a better understanding of the chemical behavior of element 164.

Elements 165 and 166. From the normal continuation of the periodic table one would expect that after the completion of a d shell (at element 164) two elements in the IB and IIB chemical groups should appear.

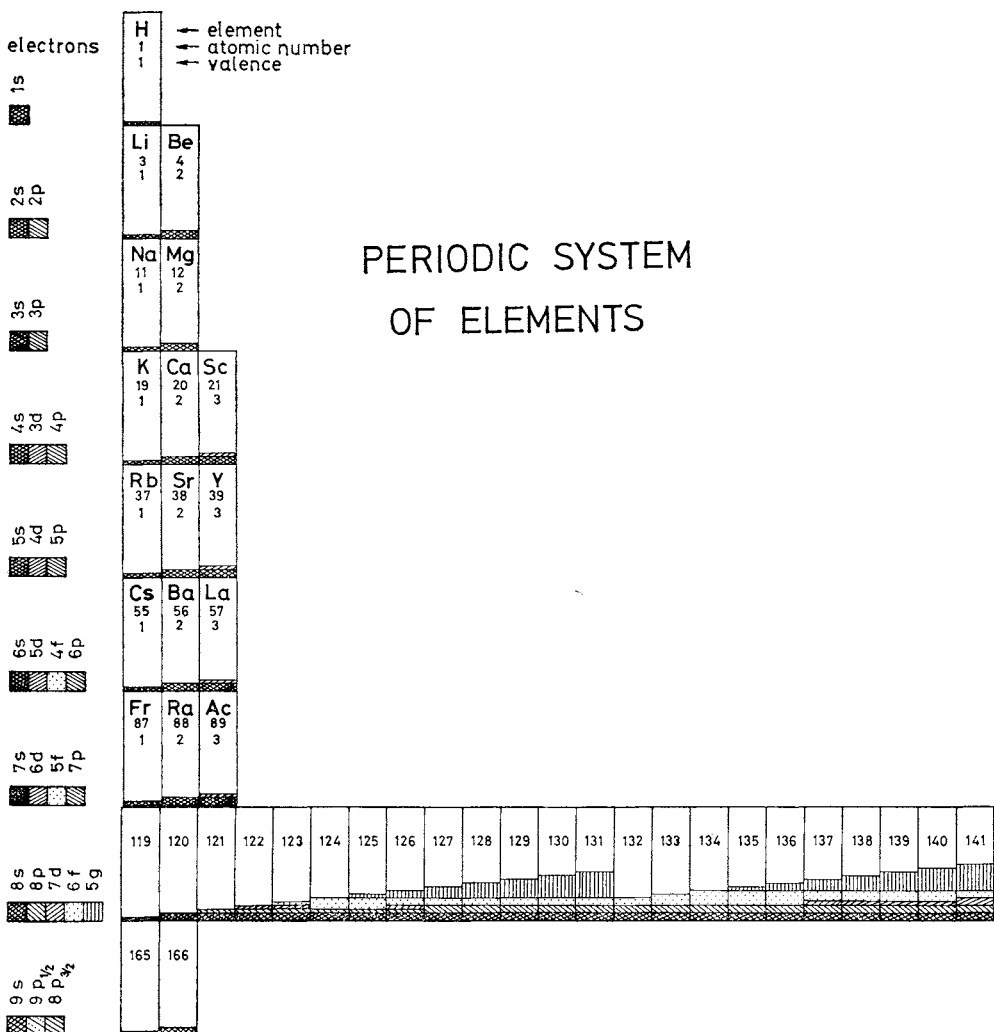


Fig. 21. The periodic system of elements continued up to element 172. The chemical symbols, atomic numbers, and oxidation states are also given. The outer electrons are drawn schematically (56)

In a very formal way this is true, because with the filling of the 9s electrons in elements 165 and 166 there are outer s electrons chemically available. On the other hand, these outer s electrons should be the ones which began with the onset of the period. The 8s electrons are already very strongly bound so that the two 9s electrons which are filled in have to be assumed to define the beginning of a new period. That this interpretation is the correct one can be seen from Fig. 23, where the first ionization energies of the IA and IIA elements are compared with the IB and IIB elements. Because of the result shown in Fig. 23, we certainly include these two elements in the chemical groups of the alkali and alkaline earth

																		He 2 0															
																		B 5 3	C 6 4,2,4	N 7 -3,2,5	O 8 -2	F 9 -1	Ne 10 0										
																		Al 13 3	Si 14 4	P 15 5,3,3	S 16 6,4,-2	Cl 17 -1,5	Ar 18 0										
																		Ti 22 4,3	V 23 5,4,2	Cr 24 3,6,2	Mn 25 2,3,4,6,7	Fe 26 3,2	Co 27 2,3	Ni 28 2,3	Cu 29 2,1	Zn 30 2	Ga 31 3	Ge 32 4	As 33 3,-3,5	Se 34 4,6,-2	Br 35 -1,5	Kr 36 0	
																		Zr 40 4	Nb 41 5,3	Mo 42 6,5,3	Tc 43 7	Ru 44 3,4,6,8	Rh 45 3,4	Pd 46 2,4	Ag 47 1	Cd 48 2	In 49 3	Sn 50 4,2	Sb 51 3,5	Te 52 4,6,-2	J 53 -1,5,7	Xe 54 0	
Ce 58 3,4	Pr 59 3	Nd 60 3	Pm 61 3	Sm 62 3	Eu 63 3,2	Gd 64 3	Tb 65 3	Dy 66 3	Ho 67 3	Er 68 3	Tm 69 3	Yb 70 3,2	Lu 71 3	Hf 72 4	Ta 73 5	W 74 6	Re 75 7,4,-1	Os 76 4,6,8	Jr 77 3,4,6	Pt 78 4,2	Au 79 3,1	Hg 80 2,1	Tl 81 1,3	Pb 82 2,4	Bi 83 3,5	Po 84 2,4	At 85	Rn 86 0					
Th 90 4	Pa 91 5,4	U 92 6,5,4,3	Np 93 5,6,4,3	Pu 94 4,6,5,3	Am 95 3,4,5,6	Cm 96 3	Bk 97 3,4	Cf 98 3	Es 99 3	Fm 100 3,2	Md 101 2,3	No 102 2	Lw 103 3	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118					
142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164											
																							167	168	169	170	171	172					

metals (85). This interpretation is also supported by a study of Fig. 10, which shows the calculated radii of these elements resembling those of the elements K and Ca. This classification is, of course, not entirely, satisfactory in every respect because from a more chemical point of view these elements will also show characteristics of the IB and IIB groups because of the underlying $7d$ shell. Therefore, higher oxidation states than $+1$ and $+2$ might readily occur.

Elements 167 to 172. Between 167 and 172 the $9p_{1/2}$ and $8p_{3/2}$ electrons will be filled, and it is quite an accident that the energy eigenvalues are so close together (see Fig. 14) that a p shell will occur containing 6 electrons with virtually no

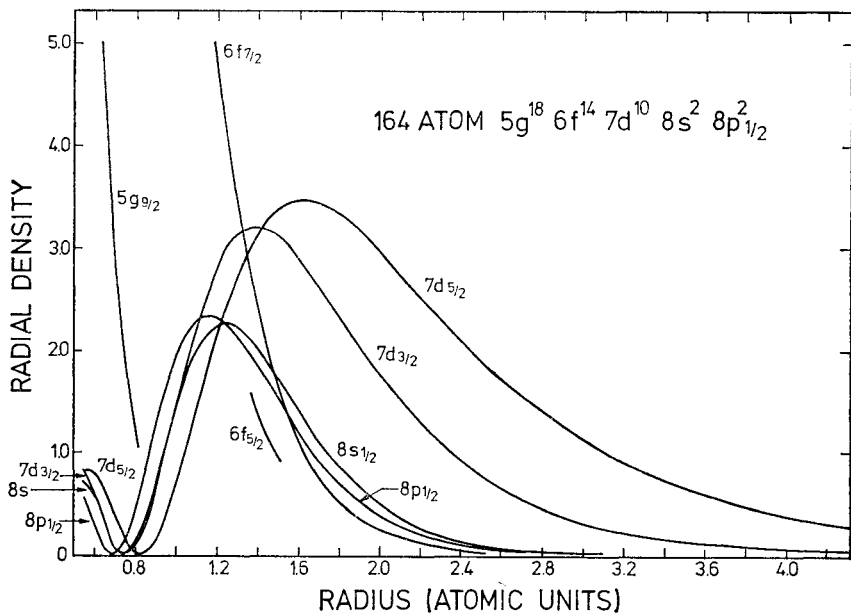


Fig. 22. Radial wave functions of the outer electrons of element 164. The $8s$ and $8p_{1/2}$ electrons are well inside the atom and thus not available for chemical bonding (55, 71)

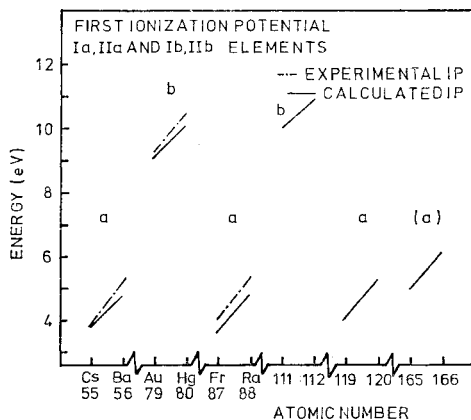


Fig. 23. First ionization energies of the IA, IIA and IB, IIB elements (85)

splitting of the subshells but different principal quantum numbers. This situation is analogous to the nonrelativistic p shell in the 3rd period. Therefore, the normal oxidation states of elements 167 to 170 will be 3 to 6. Element 171 is expected to have many possible oxidation states between -1 and $+7$, as the halogens do. Here again, the electron affinity will be high enough to form a hydrogen halide like $H(171)$. Fricke *et al.* (56) calculated a value for the electron affinity of 3.0 eV,

which is as high as the value of J^- , so that $(171)^-$ will be quite a soft base. Element 172 will be a noble gas with a closed p shell outside. The ionization energy of this element, as shown in Fig. 15, is very near to the value of Xe, so that it might be quite similar to this element. The only great difference between Xe and 172 is that element 172 is expected to be a liquid or even a solid at normal temperatures because of its large atomic weight. As indicated in connection with the noble gas 118, element 172 will tend to be a strong Lewis acid and hence compounds with F and O are expected, as has been demonstrated for xenon. In Table 6 the chemical and physical properties of elements 156 to 172 are tabulated.

Element 184. *Penneman, Mann and Jørgensen (72)* speculated about the chemistry of element 184. This must be regarded as mere speculation because (a) no calculations of nuclear stability had been made up to that time, (b) it seems to be impossible to create this nucleus with any known combination of nuclei, and (c) no calculations of the atomic behavior were available to them. Mann reported that his Dirac-Fock program was unable to go beyond $Z = 176$. Nevertheless, their speculation is quite plausible because after element 172 another extremely long transition series would start with the filling of the $6g$, $7f$, and $8d$ shells. The complication with $6h$ electronic states might also arise. These loosely bound electrons would mean that it would be very easy to reach very high oxidation states, as stated by *Penneman et al. (71)*. A model calculation of *Fricke and Waber (60)* taking into account a phenomenological formulation of quantum-electrodynamical effects makes it possible to extend the Hartree-Fock calculations to even higher elements. They found the ground-state of element 184 to be $(164)\text{core} + 9s^2 9p_{1/2}^2 8p_{3/2}^4 6g^5 7f^4 8d^3$. Because of either the small radial extension or the large binding energy, only the $8d^3$ and $7f^4$ electrons might be available for chemical bonding. The $10s$ and $10p_{1/2}$ electrons do not appear in the ground-state configuration and neither do the $6h$ electrons. So it seems that the chemical behavior of element 184 is even simpler than that of the early superactinides.

If one goes to higher oxidation states, the occupation of the $6g$ and $7f$ shells changes. The main trend is clearly an increase in the number of electrons in the $6g$ shell. The latter is radially so far inside the atom that these electrons will not be directly available for chemical bonding; instead, the $7f$ electrons will become involved. From a comparison with uranium, *Fricke and Waber (60)* conclude that a $+5$ or $+6$ oxidation state may easily be reached, whereas in aqueous solution the $+4$ oxidation state will be the most stable. Even higher oxidation states seem to be unrealistic because then the electrons from the deeply buried $6g$ shell, would have had to be removed, and their binding energy increases rapidly with higher ionization. This increase is so great that occupation of the open $6g$ shell would lead to a deoccupation of the closed $9s$ and $9p_{1/2}$ shells, beginning at 184^{+8} .

This clearly indicates that, here too, in a region of a very long transition series, where many outer electron shells are being filled simultaneously in the neutral atom, the increase in ionization energy is very like what is observed in all other elements. This means that we do not expect extremely high or very unusual oxidation states.

Table 6. Summary of predictions for elements 156 to 172. This table is taken from *Fricke and Waber (85)*

Element	156	157	158	159	160	161	162	163	164	165	166
Atomic weight	445	448	452	456	459	463	466	470	474	477	481
Chemically most analogous group		IIIB	IVB	VB	VIB	VII B	VIII	VIII	VIII	IA	IIA
Outer electrons	$7d^2$	$7d^3$	$7d^4$	$7d^4 9s^1$	$7d^5 9s^1$	$7d^6 9s^1$	$7d^8$	$7d^9$	$7d^{10}$	$9s^1$	$9s^2$
Most probable oxidation state	+ 2	+ 3	+ 4	+ 1	+ 2	+ 3	+ 4	+ 5	+ 2,4,6	+ 1,3	+ 2
Ionization potential (eV)	3.7	4.8	5.7	3.8	4.1	4.5	5.4	6.0	6.8	5.0	6.1
Metallic radius (Å)	1.7	1.63	1.57	1.52	1.48	1.48	1.49	1.52	1.58	2.1	1.8
Density (g/cm ³)	26	28	30	33	36	40	45	47	46	7	11
Element	167		168		169		170		171		172
Atomic weight	485		489		493		496		500		504
Chemically most analogous group	IIIA		IVA		VA		VIA		halogen		noble gas
Outer electrons	$9s^2 9p_{1/2}^1$		$9s^2 9p_{1/2}^2$		$9s^2 9p_{1/2}^2 8p_{3/2}^1$		$9s^2 9p_{1/2}^2 8p_{3/2}^2$		$9s^2 9p_{1/2}^2 8p_{3/2}^3$		$9s^2 9p_{1/2}^2 8p_{3/2}^4$
Most probable oxidation state	+ 3		+ 4		+ 5		+ 6		+ 7,3, - 1		0,4,6,8
Ionization potential (eV)	6.4		7.5		8.3		9.2		10.2		11.3
Atomic radius (Å)	1.58		1.48		1.39		1.35		1.27		1.22
Density (g/cm ³)	17		19		18		17		16		9

V. Critical Analysis of the Predictions

The predictions of the physical properties and chemical behavior of the super-heavy elements reviewed here can only be a starting point for chemical studies in this region of elements. Nevertheless, it seems very possible that the predictions will not be too far away from reality, at least for the elements up to $Z = 120$. In this region one is still close enough to the part of the periodic system with known elements so that the combination of the simple continuation of trends in the chemical groups together with the results of the very credible calculations, tested in the known part of the elements, will produce quite good predictions about the physical and chemical behavior of superheavy elements. Neither the relativistic effects nor the additional uncertainties will be so large as to create really unexpected new situations.

This statement is rather less true for the elements beyond element 120. In the superactinides we have the unknown chemical behavior of five quite loosely bound and strongly mixed shells together with the unknown chemical behavior of g electrons, and in the region beyond that the structure of the outer electron shells has changed so drastically that only conclusions drawn by analogy can give some idea of the chemical behavior. Even the classification of these elements into chemically analogous groups is not straightforward, so that in constructing the continuation of the periodic table one has to use either more formal or more chemical arguments. In the continuation of the periodic system shown in Fig. 21 we have tried to include both types of argument.

The predictions of the chemical behavior of the elements in the vicinity of the second quasi-stable island are supported only by the calculations within the Hartree-Fock model. The main question in this connection is whether the single-particle Dirac equation is still a good equation for very heavy elements with many electrons and $Z > 137$. That this is true, at least up to $Z = 100$, has been shown by *Fricke, Desclaux and Waber (105)*. By taking into account the extended nucleus, a formal solution of the Dirac equation is possible up to $Z = 175$. At this point the $1s$ level drops into the continuum of electrons with negative energy. In addition, the interaction between the bound levels and the vacuum becomes so large that the bound electrons and the whole vacuum have to be treated together, as was done theoretically by *Reinhardt et al. (106)*. This calculation includes the quantum-electrodynamical effects of vacuum polarization and fluctuation. Also, the effect of retardation in the Coulomb interaction, the magnetic interaction and correlation should be included, in addition, for very large Z elements in an exact manner. All these additional contributions are presently under investigation, but no exact results have been given yet for these very high Z elements. Nevertheless, in the region of the first quasi-stable island these effects are not expected to change the chemical behavior of the elements. The only differences one would expect are some small changes in the binding energy of the $j = 1/2$ electrons. The changes in the

region of the second quasi-stable island of stability might be larger, however. A first heuristic study was done by *Fricke (61)* and *Fricke and Waber (60)* by changing the potential near the nucleus, where most of the effects are expected to be maximal, so drastically that the energy eigenvalue of the $1s$ state was raised by about 30%. Although this change was very large, the filling of the outer electron shells was only affected (60) at the elements 161, 162 and 167 to 172, where the $8p_{3/2}$ and $9p_{1/2}$ shells are filled in the opposite order in the extended calculation. But even this does not change the chemistry significantly. Thus these results may be taken as a first indication that the calculations done within the approximation used in this article can also be quite valuable for the very heavy elements, and that the coupling between the behavior of the inner electrons and the valence electrons is quite small.

VI. Application of the Chemical Predictions

The predictions of the chemical properties of the superheavy elements discussed in Section IV make it possible to design experiments for their chemical identification should they be produced by heavy-ion bombardement. A few simple preliminary experiments have been performed, utilizing the tandem cyclotron combination at Dubna and the SuperHILAC at Berkeley.

Flerov, Oganessian and coworkers (107) at Dubna have bombarded uranium with xenon ions and chemically isolated fractions containing the acid-insoluble sulfides of carrier elements, which behave like osmium through bismuth and are the chemical homologs of the superheavy elements 108 to 115. Because the sulfides of these elements are expected to be insoluble in acid solution, it was expected that these superheavy elements would be present in these carrier fractions, but only a few spontaneous fission events were observed in the sulfide fraction, thus giving no evidence of superheavy elements. At Berkeley, *Kratz, Liljenzin* and *Seaborg* (94) have made chemical separations designed to isolate the superheavy elements following bombardment of uranium with argon and krypton ions. Their chemical separations were based on the expected marked tendency of the superheavy elements to form strong complex ions. Especially the elements in the range from 109 to 115 should be soft acceptor ions, as discussed in Section IV, and are expected to form strong complex ions with heavy halide ions such as bromide and iodide, in contrast to the hard acceptors such as the lanthanoid and actinoid ions. They form much weaker complex ions (with essentially electrostatic bonding) with these halide ions. This should provide the means for the separation of such superheavy elements from the lanthanoids and actinoids. As discussed in the section on the elements near 112, these elements are expected to form stable iodide and bromide complex ions, which could actually be used in the separation. Thus the separation problem is reduced to a separation of anions from cations, which can be achieved by (1) cation exchange, (2) solvent extraction with aliphatic amines, and (3) ion exchange.

Keeping in mind that one will have to deal with one atom at a time, one obviously thinks of chromatographic techniques where the separation step is repeated many times and where one can expect even a single atom to behave statistically just like a macroamount of the same substance. The three above-mentioned techniques have been tested in chromatographic columns using radioactive tracers of a variety of elements. The best results were obtained with the cation-exchange procedure. In addition, separation steps for groups of elements have been added by using different volatilities from HBr/Br₂ solutions and the different degree of complexing with bromide and chloride ions.

On the basis of these predictions, the chemical separation scheme shown in Fig. 24 has been utilized on thick uranium targets bombarded with argon and krypton ions. With a few exceptions (bromine, iodine, arsenic), no carrier material

**CHEMICAL PROCESSING OF HEAVY-ION BOMBARDED
URANIUM TARGETS**

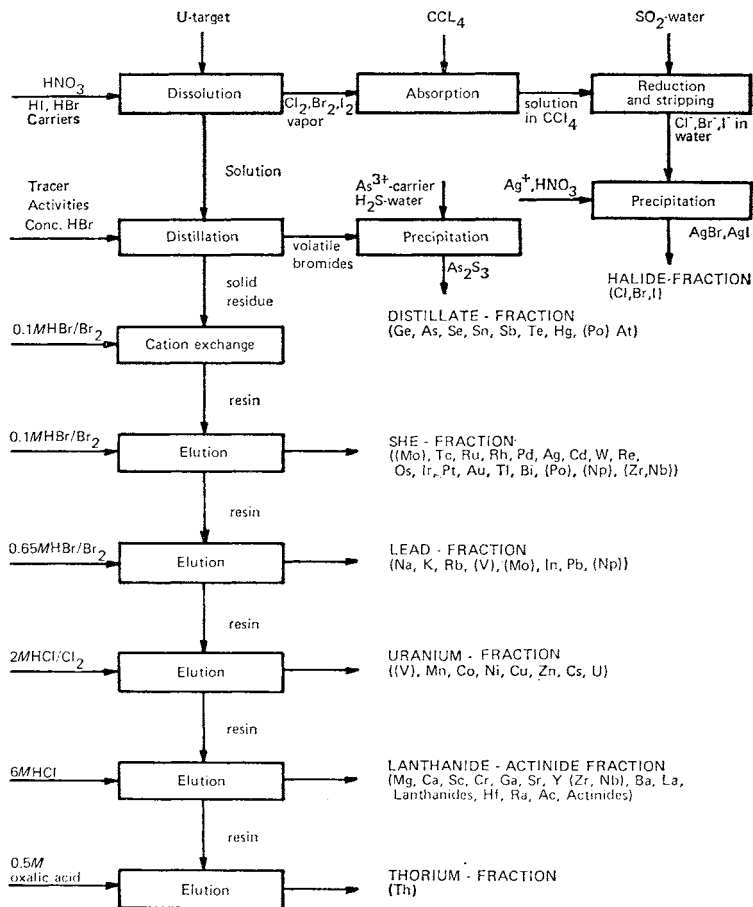


Fig. 24. Chemical processing of heavy-ion bombarded uranium targets as used by Kratz and coworkers (94). Elements 112 and 114 are expected to appear in fractions separated from the main group of superheavy elements.

was added, *i.e.* carrier-free chemical separations were made leading to the desired thin fractions for measuring α and spontaneous-fission radioactivities. Actually, the details of this separation scheme are such that mercury and lead, presumably acting as prototypes for elements 112 and 114, appear in fractions separated from the main group of superheavy elements and its prototype elements.

When the chemically isolated fractions, which correspond to the superheavy elements, were examined with respect to the detection of possible decay by spontaneous fission and alpha emission, no evidence of such decay was found, thus indicating the absence of superheavy elements. Since this scheme corresponds

to a formation cross-section of less than 10^{-35} cm² for an assumed half-life of 100 days, the result is not surprising, because the indicated nuclear reactions are not those considered best suited to the synthesis of superheavy elements.

The expectation that superheavy elements will be detected by chemical and other identification procedures, even with these very small-cross sections, is now shifting to the heavy-ion accelerator laboratory (GSI) in Germany. There is the hope that the use of other heavy ions (including ions up to uranium) and greater beam intensities will lead to the synthesis and identification of superheavy elements. There are also several groups associated with GSI presently developing setups to detect superheavy elements using chemical separation methods similar to those described above as well as phase separations.

Speaking generally, one might say that we are just at the beginning of this field of study. We have a very preliminary idea of what we might expect to find in this large white area of the periodic table. We are sure that a large variety of new phenomena reported from the nuclear physics, atomic physics and chemical points of view will make this field a more and more interesting one.

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VII. References

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