

IONS OF THE SUPERHEAVY ELEMENTS IN VACUUM AND IN SOLUTION*

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Abstract—The extension of the Periodic Table into the range of unknown atomic numbers of above one hundred requires relativistic calculations. The results of the latter are used to indicate probable values for X-ray transition lines which will be useful for identification of the atomic species formed during collision between accelerated ions and the target. If the half-lives of the isotopes are long, then the chemistry of these new species becomes an important question which is reviewed for E110, E111 and E112.

The possible structural chemistry of the elements E108 to E112 is suggested.

Finally the effects of solvation on ions of the actinide and superheavy elements have been studied.

PREDICTIONS CONCERNING SUPERHEAVY ELEMENTS

THE GENERAL problem of superheavy elements has become more restricted and better defined than it was six years ago. At that time, the possibility of forming a large number of elements beyond the three known elements Lawrencium (E103), Rutherfordium or Khurchatovium (E104) and Hahnium or Nielsborhrium (E105) was worth considering. In a recent monograph[1] Plerov and Zvara have presented their claims that they isolated some isotopes of the latter two elements before Ghiorso and his colleagues in the University of California did,‡ but the latter have impressive data.

Even though the possibility of very many synthetic elements seemed very slim, we tried to establish the chemical behavior of elements with atomic numbers as high as 184 in a series of papers[2–5]. By the time the work was well underway in 1968, it was clear that only a relatively few new elements near the Islands of Stability (associated with magic proton and magic neutron numbers) were likely to have appreciable half-lives.

We devoted a considerable amount of effort to the region around $Z = 126$ particularly since there were some interesting questions about the occupation numbers of electronic states associated with a new transition series based on $(5g_{7/2}^2)$ and $(5g_{9/2}^2)$ electronic orbitals. It was a very time consuming

set of calculations since there were four incomplete shells to be considered. This search around E126 was initially motivated by the simple idea that the magic proton number would be the same as that for the neutrons, namely 126, just as it was for moderately heavy nuclei.

Then it came to our attention that the electrostatic repulsion between protons would alter the ordering of the nucleon levels. Despite this fact, we persisted in our studies near 126 because the nuclear calculations of many authors, for example, Murah, *et al.* as reported by Greiner[6] showed only one proton state, namely the $(3p_{3/2}^1)$ state, in the energy gap between $(2f_{7/2}^5)$ level with 124 protons and $(2g_{9/2}^2)$ level with 34 protons. If the position of the $(3p_{3/2}^1)$ level were near the upper one of these, the nuclear stability of 126 protons might still have been significant. More recent work[7] has made it clear that isotopes of E126 would have very short half-lives. We have abandoned any further work in this region for the present.

Several years ago the possibility of making elements near the second or more remote Island of Stability, i.e. near $Z = 164$ by combining two nuclei of elements near lead was considered. The name “Zweiblei” was humorously suggested by Penneman[8]. However, no two elements possess a sufficient number of neutrons to lead to the magic neutron number 324 required to insure a reasonable stability of the united nucleus. The possibility of a three or four neutron rich nuclei colliding simultaneously seems far too remote to be considered seriously.

Thus the broad original goal of looking for many elements has been considerably narrowed to an investigation of a few elements near the more accessible Island. In the Fig. 1 taken from the recent paper by Fiset and Nix[7], a few isotopes in

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‡Consequently, they claim the right to name these two elements. Eventually this question will be settled by the IUPAC Commission on Nomenclature of Inorganic Chemistry.

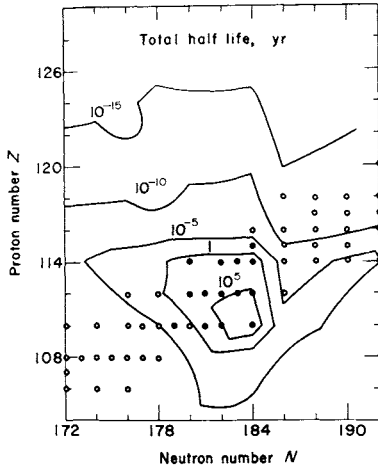


Fig. 1. Contour lines representing the combined effects of various decay modes on the half-lives of various superheavy nuclei (after Fiset and Nix [7].)

the range of 109–112 protons and 182–185 neutrons are predicted to have total half-lives approaching 100,000 years.

If the alpha emission of $^{293}\text{E112}$ or of $^{289}\text{E110}$ were the only mode of decay, the former element would be roughly as radioactive as ^{239}Pu . The alpha particles would be much “harder”, i.e. more energetic. However, spontaneous fission appears to be the principal rapid mode of decay as Fig. 2, which is also taken from their paper, shows. This being true, one would have only a very radioactive isotopes of element E110. These two graphs were derived using a diffuse-surface, single particle nuclear Hamiltonian. The latter method appears to this lecturer to be more reliable than the various forms of harmonic oscillator potentials used so successfully by Nilsson[9] and by Strutinsky[10].

It now seems reasonable to concentrate our attention on the elements in the range E109–E112, which is a much more restricted task than the one upon which we embarked six years ago. Of course, one can not be completely certain of predicted half lives, so we must consider two alternatives in this lecture. One is that the half-life of any isotope which will be produced in the vicinity of E110 might only amount to a fraction of a year. The second alternative is that it might have a half life several orders of magnitude longer than one year. In the first case, one would be forced to identify the element by its radioactive decay, perhaps by its alpha emission spectra and by the X-rays produced by various Auger processes. The chemistry of such an element would be of only academic interest, since separating the few elements from the matrix might be too slow. Most efforts would probably be centered around using mass spectrometers. Various measurements might be attempted during the time of flight.

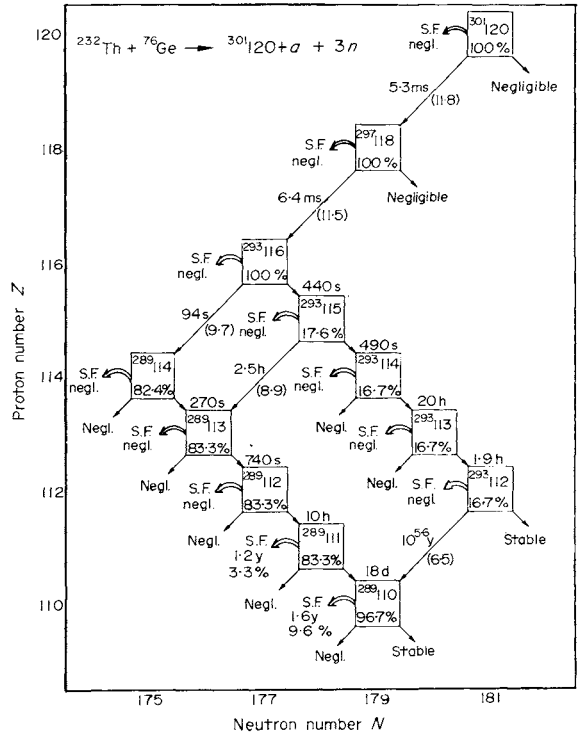


Fig. 2. One of the decay chains starting with E122 which might be involved in producing superheavy elements (after Fiset and Nix [7]).

However, in the second instance, the element in question might be about as stable as natural uranium. Then a scheme of chemical separations would become of major importance and the detailed chemistry of such elements would be invaluable in developing separation methods.

Both of these approaches will be taken in this lecture. In what follows, I will take up first, the general problem of the collision between bombarding and target ions and what X-rays might be effective in identifying the few superheavy elements. In the second portion I will discuss information about the ground state of various elements and their ions as determined in *jj* coupling. Next some attention will be devoted to the solution chemistry of heavy and superheavy elements.

I. COLLISION PROCESSES

In this discussion of collision between ions, I will not attempt to describe the process of fusing the two nuclei together. There are others who are eminently more qualified than I am to discuss the nuclear problems.

The aspect which is of some interest is what happens to the electrons during the early stages of the process. The usual treatments of atom-atom scattering[11] which occur in the literature have

been associated with chemical reactions and the range of kinetic energies such research workers have in mind are thermal energies and certainly less than 0.1 eV. In the fusion studies, the kinetic energies are orders of magnitudes larger and may approach 2 GeV.

Betz[12] and his colleagues have studied the ionization of gas atoms and molecules when, for example, Iodine ions have been accelerated up to 46 MeV. Energetic heavy ions are stripped of most of the outer electrons by the target atoms. Even when some of the ejected electrons are recaptured by the ion, they are bound only in very excited states and easily lost. Approximately 20 per cent of the atoms in their experiments were found as ions with thirteen positive charges. In another experiment, a beam of ^{127}I ions was accelerated to 74.5 MeV and used to bombard Hg vapor; about 20 per cent of the I atoms had lost 13 electrons and approximately 1 per cent had lost as many as 20 electrons. They point out that "Dissipation of ion excitations... (by radiative processes) ... can be neglected." An electron captured into an excited state will be lost from the same state "... and capture and loss processes will compete." There are some important differences between the theoretical model of Bohr and Lindhard[13] and the findings of Betz and Grodzins[14]; the reader is referred to these references.

Some specific details are useful for our understanding later. The average charge $q(\nu)$ which the fragments acquire depends on the ratio of the velocity ν of projectile ion to velocity ν_0 of the most loosely bound electron. Dmitriev and Nickolaev[15] proposed the first relation in 1964, namely

$$\bar{q}/Z = A\nu/\sqrt{Z}. \quad (1)$$

A more reliable semi-empirical relation is

$$\bar{q}/Z = 1 - C \exp(-\nu/\nu_0 Z^\gamma) \quad (2)$$

where the two constants, C is slightly larger than unity and γ is approximately two-thirds. Specific data quoted by Betz *et al.*[12] for uranium, bromine and iodine ions with energies up to 180 MeV striking various forms of targets give $C = 1.034$ and the exponent in the reduced velocity as $\gamma = 0.688$. It is interesting that the average equilibrium charge is only slightly higher in a solid than in a gaseous target. The ratio \bar{q}/Z is not observed to exceed 0.4 in heavy ions and this ratio increases rather slowly with the collision velocity. In iodine, when 25 electrons have been removed from the atom, all the electrons in the N shell have been removed and energy must be supplied to create holes into the M shell and eject these electrons. Some promotion of electrons into unfilled outer orbitals is possible and these will decay by various Auger processes after the ion fragments have left the target area.

At an energy of 8 MeV per nucleon which is design goal in several planned accelerators, the energy to which the linear accelerators would accelerate uranium ions is 1.904 GeV. The stripping experiments of Betz *et al.* have already been carried out at an energy of only one order of magnitude smaller namely, at 0.18 GeV.

The spread d of the charge distribution of the stripped ions (roughly the width at half height) has been found to be relatively narrow and insensitive to velocity. Using the approximate formula of Betz and Smeltzer[16]

$$d = 0.27Z^{1/2}. \quad (3)$$

d would range from 2.7 to 3.0 for the superheavy elements. The fraction of the ions with $(\bar{q} + 3d)$ electrons removed, would be two orders of magnitude smaller than the percentage at \bar{q} .

For safety, let us assume that \bar{q}/Z may be as high as 0.46 although this fraction is larger than would extrapolated by means of equation (2). Similarly, let us assume then that d is as large as 4. On this basis we would estimate that about 1 per cent of the ions might have as many as 54 electrons removed (i.e. a value of $\bar{q} + 2d$).

The different non-equilibrium behavior of \bar{q} in the Bohr-Lindhard (BL) and Betz-Grodzins (BG) treatments is indicated in Fig. 3. The implication of this schematic drawing of \bar{q} for a solid in Fig. 3 is that during the non-equilibrium process the ionic charge will increase from \bar{q}_s to \bar{q}_s after the fragments have left the target. The non-equilibrium competition between ionization and electron capture processes may not go as indicated by this drawing. Apparently no investigation has been conducted to ascertain whether \bar{q} does change in this region beyond the target. However, the possibility that \bar{q} may change during the flight of the ionic fragments has been retained rather than a single time-independent value, since the values of \bar{q} will influence the X-rays which are emitted.

Need for relativistic atomic calculations

In 1960, Fröman[17] studied the influence of

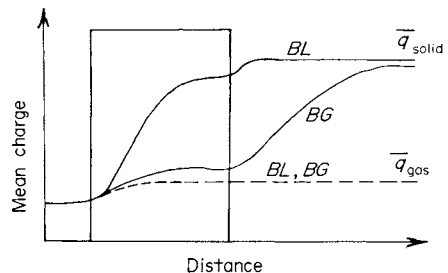


Fig. 3. A schematic drawing showing the possible variation in the average number of electrons removed \bar{q} when an energetic ion strikes a solid or gaseous target (after Betz and Grodzins[14]).

relativistic effects on the total energy atoms and ions. As a guiding rule, the relativistic terms become dominant when the expectation values of electronic interaction namely the direct and exchange energy, become small in comparison with the spin-orbit coupling energy. The electrostatic energy J and the exchange energy K are roughly proportional to Z whereas the spin-orbit energy varies roughly as Z^4 . The dominance of the spin-orbit interaction occurs at about $Z = 40$ for isoelectronic series of 2-electron atoms and ions. For the isoelectronic series, Ne, Na^+ , Ca^{2+} . . . , it sets in [17] about $Z = 65$. The Hydrogenic value of the spin-orbit energy is approximately given by

$$\zeta_{nl} = \frac{Z^4}{n^3 l(l + \frac{1}{2})(l + 1)c^2} \quad (4)$$

where n is the principal quantum number, l the angular momentum and c the speed of light. Atomic units where $m = e = \hbar = 1$ have been assumed for most formulas.

The traditional approach for chemists is LS coupling. This is partly because of its success in dealing with light elements. The point is frequently made that even the valence electrons in a superheavy element experience only a very small field.

When energies J and K are large, a perturbation treatment of spin-orbit coupling is not adequate because we are dealing with core electrons and their wave functions are influenced by the strong field. Thus we must start with jj coupling rather than start with LS coupling and append to it a correction to only the valence electrons for this relativistic effect. The two coupling schemes lead to different results. For example, Hund's rule must be expanded to predict the ground states in relativistic jj coupling.

2. QUASI-MOLECULAR SPECIES

Suppose that the collision between two nuclei is not successful in bringing about fusion. For a very brief period, a quasi-molecular state will exist during which time the remaining electrons will experience a nuclear field which is somewhere between that of the compound nucleus and that of a diatomic molecule. How such a field would influence the electronic levels and hence X-ray lines during its lifetime or flight is an interesting subject.

Correlation diagrams were pioneered by Hund [18] and Mulliken [19] in 1927. These diagrams illustrate on one side the energy levels of the two separated atoms. The constituent atoms were imagined to approach each other until physically realistic molecules are formed. The atoms are permitted to continue to approach each other "...until the physically impossible process of

nuclear coalescence" occurred [20]. The atomic levels of "...resulting united atoms were once again known [20]. " Levels of the same symmetry and l -values are connected. The energy levels are classified by their symmetry with respect to rotation around the internuclear line into "gerade" and "ungerade" states. However we will not use these distinctions in the accompanying graphs.

One connects levels in Fig. 4 with the same j -values to study the formation of quasimolecular species. In the atomic levels, the degeneracy of a given state is $(2j + 1)$. As one connects levels on the two sides of the diagram, whether an intersection occurs or not, is dictated by the degeneracy of similar atomic levels. That is, except for states of different symmetry, the degeneracy of a level cannot be increased beyond the $(2j + 1)$ -value. This is a characteristic of the angular dependence of the molecular orbital. Here Ω is angular momentum projected on the internuclear line. Crossing of two lines that have the same symmetry would increase that number; hence it would be forbidden. A further restriction is that there can be no change in the number of radial nodes, hence certain states with the same j cannot be connected even though it might be energetically desirable. Accidental de-

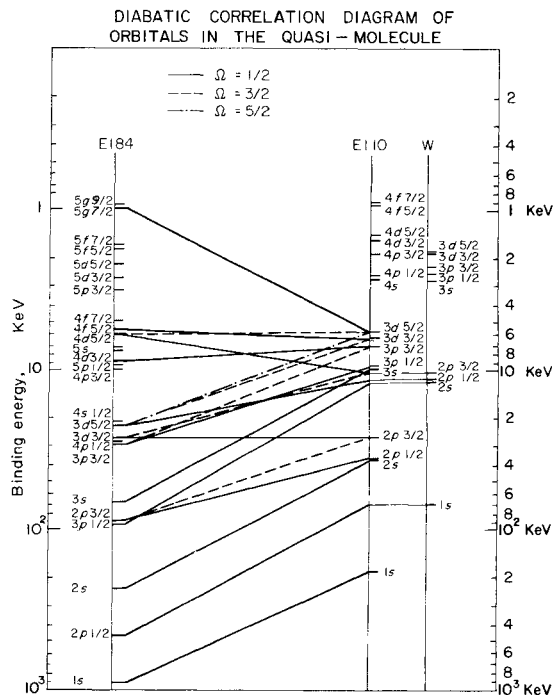


Fig. 4. Correlation diagram for the diabatic form of a highly ionized quasi-molecule. Each line corresponds to two electrons. The number of radial nodes $n - |\kappa|$ and the projection Ω of the angular momentum j are conserved along lines joining $|nlj\rangle$ states. (After Fricke and Waber [25]).

generacies caused by the intersection of lines of different symmetry however are acceptable in the correlation diagrams.

In Fig. 4 we are talking about degeneracy associated with the rotational symmetry of the atomic orbital $|jm_j\rangle$. We will let the internuclear line correspond to the Z axis and call the projection of the angular momentum on this line Ω as Armbruster *et al.*[21] did. They did not illustrate the relevant molecular orbitals which involve two linear combinations of $|2p_A \frac{1}{2}\rangle$ and $|2p_B \frac{1}{2}\rangle$ to form gerade and ungerade functions such as occur in Molecular Orbital theory.

The non-relativistic correlation diagram which Armbruster *et al.*[21] gave does incorporate many of the features which are needed to illustrate energy transitions. Nevertheless, it is not satisfactory for calculating the energy transitions, because they approximated the energy levels and introduced spin-orbit coupling as a perturbation to LS coupling. However, the most serious problem in terms of deducing any energies is that Armbruster *et al.*[21] chose the very unlikely united atom E199 and extrapolated the non-relativistic Herman-Skillman energies [22] from approximately $Z = 100$ to $Z = 199$. Using advanced forms of the relativistic treatment, Fricke and Waber have succeeded [23] in doing E184 whereas using either the earlier relativistic Dirac-Slater or even Mann's Dirac-Fock program [24], it has only been possible to converge E175 and then with considerable difficulty. The earlier calculations ignore vacuum fluctuations [24].

As Fricke and Waber [25] point out in a recent paper that $Z = 190$ the $(1s \frac{1}{2})$ $(2s \frac{1}{2})$ and even $(2p \frac{1}{2})$ electrons will have energies comparable or lower than those in the filled continuum of states with negative frequencies, states in Dirac's sea of negative energies. Whether pair production or other phenomena will limit the electrical field is not known in detail.

Figure 4 shows the graph drawn for a quasi-molecule composed of tungsten and E110. Only the levels for the lowest 38 states associated with W plus E110 are shown on the right. The states connected on the left can hold 36 electrons each with a binding energy of more than 6 keV. Note that because of strong relativistic effects the $(np \frac{1}{2})$ electrons are bound more tightly than the $(ns \frac{1}{2})$ states. Note that in the united atom, states $(4p \frac{1}{2})$, $(4s \frac{1}{2})$, $(4p \frac{3}{2})$, as well as $(5p \frac{1}{2})$ are unoccupied although their binding energies exceed those of the $(4d \frac{3}{2})$ electrons. The remaining connected states $(4d \frac{5}{2})$, $(4f \frac{5}{2})$ and $(5g \frac{7}{2})$ are incompletely filled and could hold an additional 20 electrons.

A more realistic drawing based on the collision process of the ^{232}Th plus ^{72}Ge to form the compound nucleus or quasi-molecule E122 has been presented on the left hand side of Fig. 5. We have also shown the levels for various ionization states of E122 and

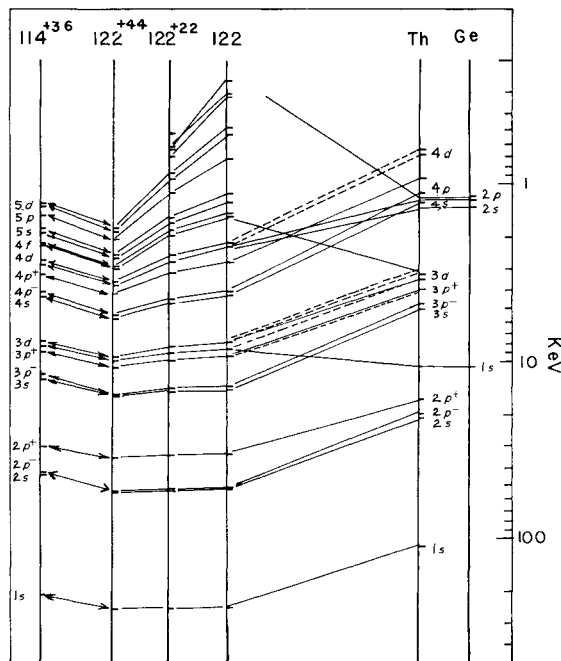


Fig. 5. An extended version of a correlation diagram which illustrates not only the lowest energy levels of the neutral E122 but the effect of ionization and of the loss of nuclear charge during radioactive decay on the analogous eigenvalues.

E114 to illustrate another feature not adequately indicated in Fig. 4.

Because the quasi-molecule would be produced by bombardment of a target, we have assumed that \bar{q}/Z might be as large as 0.36 for the illustrative purposes in making these calculations for Fig. 5.

The collision process may possibly leave holes in the $(4s \frac{1}{2})$, $(4p \frac{1}{2})$, $(4p \frac{3}{2})$, $(5s \frac{1}{2})$ and $(5p \frac{1}{2})$ levels, namely the N and O shells.

We have taken E114 as a representative element rapidly obtained by radioactive decay from the quasi-molecule based on E122. A reasonable "end" value of Z as far as the decay processes and the loss of protons illustrated in Fig. 2 are concerned is 114. That is, the half-lives to get to E116 are each shorter than 1 sec, whereas those for approaching E114 exceed 100 sec. The half lives of the daughters of E114 are significantly longer (particularly if they are rich in neutrons).

Fricke and Waber [25] calculated the (nlj) levels of E114 for the ionization states up to 54 which corresponds to a mean charge fraction \bar{q}/Z of 0.40 plus a $2d$ deviation of 8 electrons. Then we investigated the effect of ionization on various transition energies.

The various relativistic terms which contribute to making an accurate calculation and obtaining good experimental agreement for the $1s$ level in Fermium is illustrated in Fig. 6. These results due to

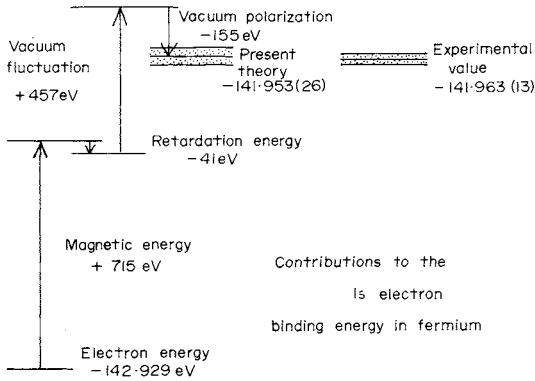


Fig. 6. Illustration of the various relativistic corrections to the energy eigenvalue of the $1s$ electron in Fermium (after Desclaux, Fricke and Waber[26].) The agreement is to within 10 eV. In an independent calculation Potter *et al.*[27] reported ± 4 eV.

Desclaux *et al.*[26] are similar to the independent calculations of Freedman, Porter and Mann[27]. Without vacuum polarization and Breit terms, the accuracy of a predicted $1s$ level is only 2 per cent. Smaller similar corrections must be applied to obtain $(2p_{1/2})$ and $(2p_{3/2})$ levels accurately.

Armbruster *et al.*[21] states "... the collision induced M spectrum may be very simple and that the shift may not be too large. Therefore an unambiguous nuclear charge determination seems to be possible." Much of their reasoning is based on the symmetry induced promotion of the $(3d_{5/2})$ electrons to the $(5g_{7/2})$ level as illustrated in our Fig. 4. Since the kinetic velocity would exceed the reduced orbital velocity ($v_0 Z^{2/3}$) for the latter state, these two electrons would be readily stripped. We agree that M shell X-rays may be induced by such a process. However, the ability to determine the atomic number of the newly formed superheavy elements is open to question. As indicated schematically, the BG curve in Fig. 3 the value of \bar{q} may be time dependent and the removal of outer electrons does influence the energy of deep core levels.

Call ΔE_1 the effect on the X-ray transition energies of as many of 54 outer electrons being stripped from neutral E114 atoms and ΔE_2 the effect of losing one proton from the nucleus to form E113. The results are summarized in Table 1 in the form of a ratio. The ratio $\Delta E_1/\Delta E_2$ indicates the feasibility of determining Z independent of the value of either \bar{q} or d .

It is clear that the effect of electron screening on the K -levels is small in comparison to effect of nuclear charge. To be able to use M shell X-rays for the determination of Z as Armbruster *et al.*[21] suggest, one will require very careful experimental work to resolve the fine structure in the X-ray lines. The task will be compounded since the natural line width is the order of several keV. The energy difference between the two transitions $4p_{3/2} \rightarrow 3d_{5/2}$

Table 1. Sensitivity of X-ray energies to a change in nuclear charge

Empty shell	Transition	$\Delta E_1/\Delta E_2$
K shell	$2p_{3/2} \rightarrow 1s_{1/2}$	0.012
L shell	$3d_{5/2} \rightarrow 2p_{3/2}$	0.170
M shell	$4f_{7/2} \rightarrow 3d_{5/2}$	1.06
	$4p_{3/2} \rightarrow 3d_{5/2}$	1.41
N shell	$5p_{3/2} \rightarrow 4d_{5/2}$	> 5*

*The calculation is for only 36 electrons removed.

and $4f_{7/2} \rightarrow 3d_{5/2}$ is 1.06 keV. The lines will be also broadened by the further possibility that several nuclear charges may be present as daughters of the radioactive decay chain. To summarize, it may be possible to determine Z without knowing \bar{q} by means of L shell X-rays but the use of M X-rays for this purpose would appear to be very difficult.

If the elements in the range of $Z = 108-112$ are more stable than treated so far (half-lives being a small fraction of a year) it is appropriate to discuss the periodic table and the chemistry of such superheavy elements. An important aspect of this is the ease with which certain electrons may be removed.

IONIZATION AND ELECTRON REMOVAL FROM SUPERHEAVY ELEMENTS

It is recognized that a lone pair of electrons occurs with considerable stability in heavy elements. One way this fact influences the chemistry of elements is in the monovalent and trivalent forms of thallium. As the Fig. 7 taken from Fricke and Waber[6] shows, the binding energy of the two $7s$ electrons is greater than that of electrons in the penultimate orbital ($6d_{5/2}$). The ionization of even one of the $7s$ electrons exceeds that of a d -electron, and of a $(7p_{1/2})$ electron. Thus the removal of one of the electrons from Tl and *a fortiori* from E113 yields a stable +1 valence. Presumably in forming the trivalent ion, it will be found that two $(5d_{5/2})$ electrons are removed before the second $(7s_{1/2})$ electron is lost.

A diagram for several electronic configurations of energy levels was used in a previous paper[28] which dealt with ionized elements with nuclear charges above 120. A similar graph has been presented for E110 in Fig. 8. The various panels represent different degrees of ionization and they show a rapid increase in ionization potential, i.e. the difference between lowest levels in successive panels. This analogue of platinum is predicted to have the general configuration $d^n s^2$ in the first three ionization states. One may infer that the creation of holes in the $(6d_{5/2})$ subshell reduces the interelectronic repulsion and favors keeping $(7s_{1/2})^2$ subshell closed.

This trend is supported by the data presented in

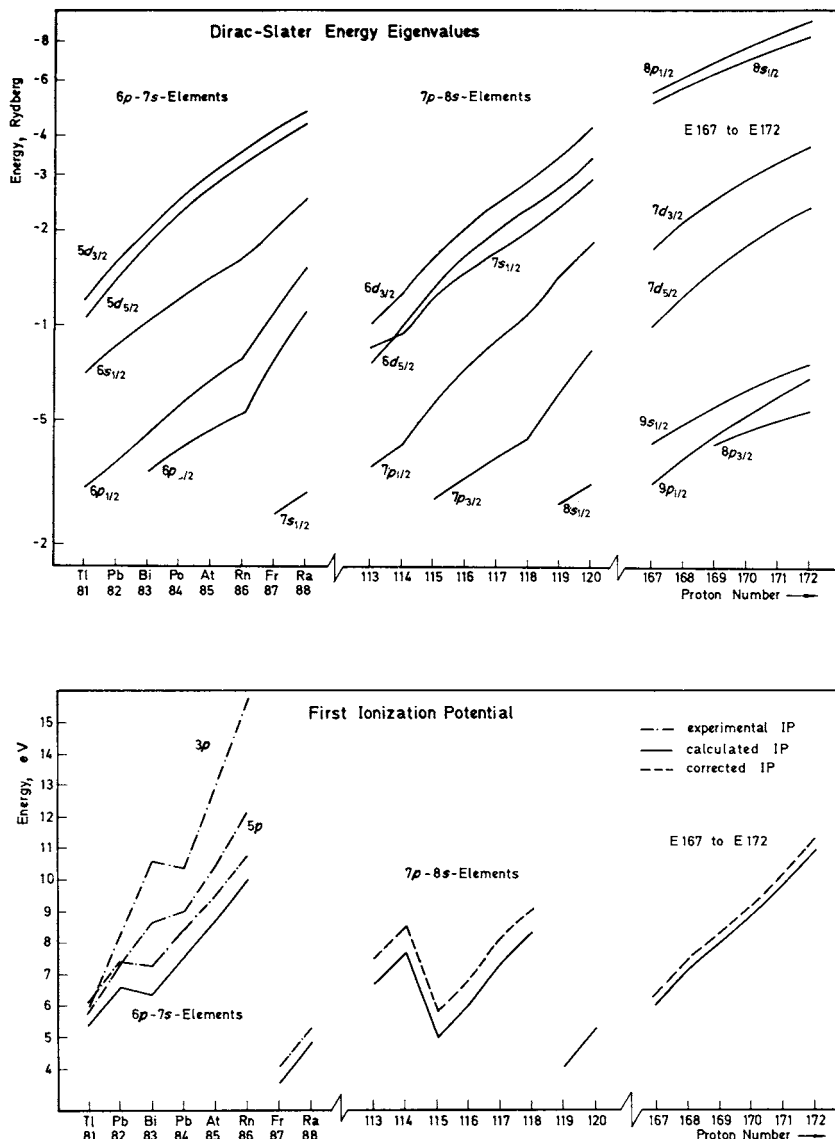


Fig. 7. Variation of ionization potentials with atomic number (after Fricke and Waber [5]).

Fig. 8 for element E111 which is analogous to gold. These calculations also indicate that the general configuration $d^n s^2$ is the lowest energy level. Only one different state $d^8 s^0$ is found for the trivalent ion of E111. The various ground state configurations are consistent with it being easier to remove up to three ($5d_{5/2}^3$) electrons than one of the ($7s_{1/2}^2$) electrons. Similar results were reported by Keller *et al.* [29].

The late Professor Cunningham estimated from thermodynamic information based on elements with lower atomic numbers, that the energy which is required for form a tetravalent ion. His values were 82, 86, 90, 94 and 98 eV, respectively for the five elements E108 to E112. Our calculations give

very comparable values for E110 and E112, namely 91 and 98 eV. A summary of his data [30] taken from the paper by Fricke and Waber [6] are presented here as Table 2.

FORMATION OF NEGATIVE IONS OF THE SUPER-ACTINIDE ELEMENTS

There is a pronounced tendency for the heavy elements to form negative ions. As mentioned in an earlier review [5] in connection with the formation of the quasi-stable negative ions of neon and argon, the closed np shell is broken and two electrons occur in the $(n+1)s$ orbitals. Presumably, part of the promotional energy comes from reducing the

Table 2. Summary of physical and chemical properties of elements E104–E112

Element	104	105	106	107	108	109	110	111	112
Atomic weight‡	272	275	277	280	282	285	288	291	294
Chemical group	IV B	V B	VI B	VII B	VIII	VIII	VIII	I B	II B
Most stable oxidation states†	+4	+5	+6	+7	+8	+6	+6	+1.3	+1.2
First ionisation potential, (eV)	5.1	6.2	7.1	6.5	7.4	8.2	9.4	10.3	11.2
Sum of first four ionis. pot., (eV)†	66	70	74	78	82	86	90	94	98
Metallic radius, (Å)†	1.66	1.47	1.41	1.39	1.37	1.38	1.40	1.46	
Density (g/cm ³)	18* 17	21.6	23.2	27.2	35* 28.6	28.2	27.4	24.4	16.8
Oxidation potential, (V)*	M → M ⁴⁺ + 4e ⁻ > 1.7								
Melting point, (°C)*	2100								
Boiling point, (°C)*	5500								
Ionic radius, (Å)†	0.75								

(After Fricke and Waber[6]).

*O. L. Keller and J. Burnet quoted by Seaborg in Mendeleev Lecture.

†B. B. Cunningham, Mendeleev Lecture.

‡Atomic weight according to Greiner *et al.*, *Z. Physik* **228**, 371 (1969).

electrostatic repulsion between the four ($np\frac{1}{2}$) electrons, by creating a hole in the subshell, and hence forming a more attractive potential for the ($n+1$) s electrons, since their repulsion is not large such negative ions are well known to form during electron capture experiments.

In connection with recent observation of negative platinum ions during photoemission by Green[31] a series of calculations were undertaken on such species. In order to bind the extra electron and cause easy convergence of the self-consistent field Dirac–Slater program, a value of the latter correction L was used which was larger than one.

The total energy of the two species of platinum ($5d\frac{5}{2}$ [6] ($6s\frac{1}{2}$)[1] and ($5d\frac{5}{2}$)[5] ($6s\frac{1}{2}$)[2] are plotted in Fig. 11, for several values of the Latter correction.

By way of justification, one may point out that Latter's correction was originally introduced to take care of the self-interaction energy of an electron in the Dirac–Slater or the Thomas–Fermi model; thus it properly has the value of unity. The present use of a larger value corresponds roughly to introducing a sphere of additional charge around an ion to stimulate its environment, as Watson[32] did in the calculation of O^{-2} ion. Without this charge, the second electron would not be bound.

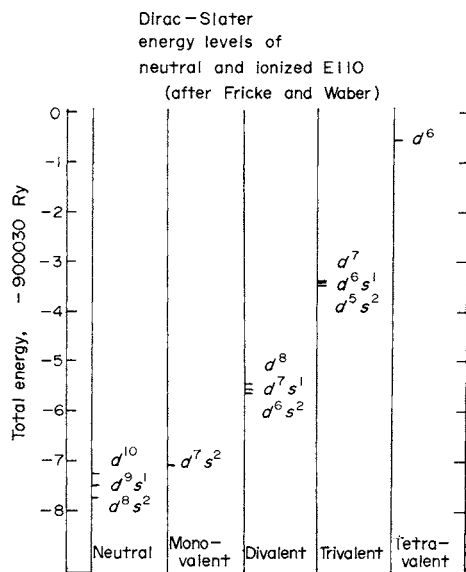


Fig. 8. Comparison of the Dirac–Slater total energies of various configurations of element E110. The displaced zero is $-90,030$ Ry.

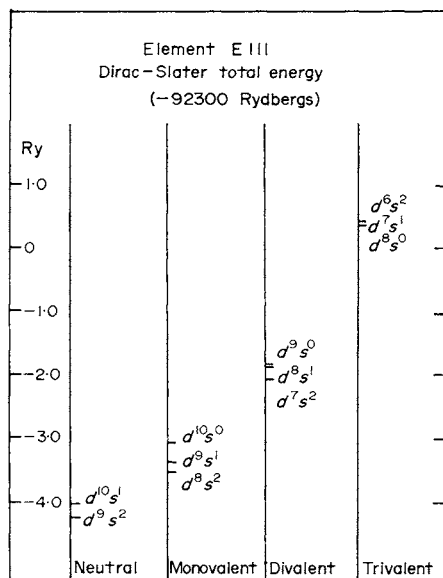


Fig. 9. Comparison of the Dirac–Slater total energy of various configurations of element E111. The displaced zero is $-92,300$ Ry (after Fricke and Waber[34]).

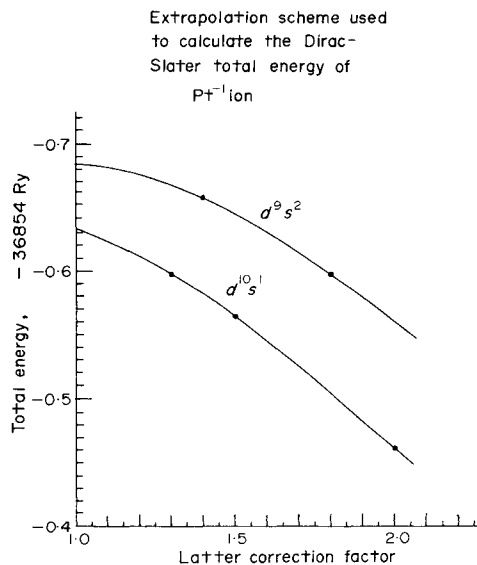


Fig. 10. Dependence of the Dirac-Slater total energy of a negative platinum ion on the value of L which is Latter's correction.

In the present case, the larger value of Latter's constant also facilitates binding of the additional electron in both species. However, it should be noted that when L approaches unity, that the configuration $(5d_{\frac{5}{2}})^6 (6s_{\frac{1}{2}})^1$ was not stable. By extrapolation of the curves in Fig. 10 to the value of $L = 1$ suggests that the energy difference between the two configurations is 0.051 Ry. As one can see, the platinum anion with the hole in the $(nd_{\frac{5}{2}})^6$ subshell is more stable than the one without. This

tendency would also hold for the formation of negative ions of E110.

The formation of negative ions of copper, silver, gold and E111 were recently investigated by Carlson and Keller[33]. The preliminary information we obtained informally is summarized:

Anion	Electron affinity (eV)
Cu^{-1}	1.0
Ag^{-1}	0.9
Au^{-1}	1.9
$(E111)^{-1}$	1.2, 1.3

They conclude "... the electron affinity of E111 is between that of Ag which does not form a 1^- ion and Au, which *does*." By now, better numbers may exist.

An independent calculation by Fricke and Waber[34] gave 1.3 eV for $(E111)^{-1}$. These confirm the ability of such elements to form anions by completing the $(ns_{\frac{1}{2}})^2$ shell. Both of these observations, the "burying" of the lone pair because of its stability and the tendency for the platinum-like E110 to develop d-holes in favor of this $(7s_{\frac{1}{2}})^2$ shell suggest that the elements will be soft in the context of Pearson's Hard-Soft Acid-Base Principle[35]. There will be a significant tendency to form covalent co-ordination compounds.

Before studying the probable covalent compounds which might be developed by the elements E108-E112, the possibility of ionic compounds with fluorine or oxide should not be neglected. With such strong electron acceptors in the vicinity of the

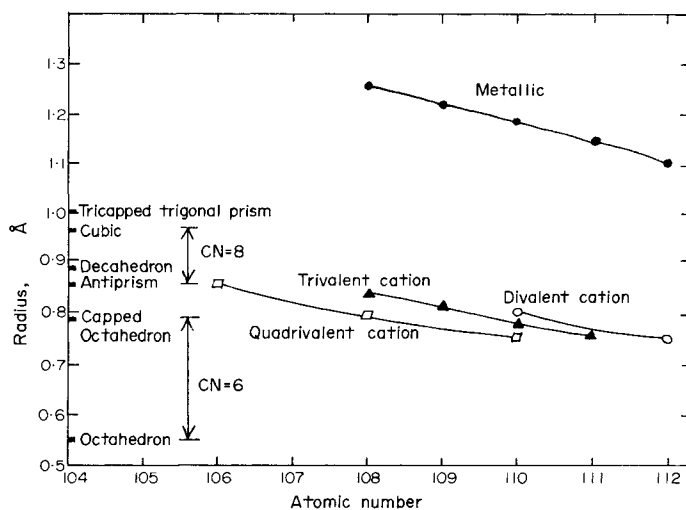


Fig. 11. Dependence of metallic and ionic radii for the platinum-like superheavy elements and the coordination numbers anticipated for poly-fluoride complexes. (Similar to graph used by Rosenweig and Penneman[36]).

central atom, strong crystal fields may develop and these will influence the availability of electrons.

STRUCTURAL CHEMISTRY OF SUPERHEAVY ELEMENTS

To establish a basis for considering this topic, let us briefly summarize the structural experience with the lanthanide and actinide ions in terms of forming polyfluoride compounds. Penneman *et al.*[36] recently gave a set of limits for the maximum coordination number observed. The reader is referred to that critical review.

The actinide compounds may involve substantially ionic bonds. There are a large variety of coordination geometries which seem to be determined largely by packing consideration. That is, despite the high charge of 4–6 which may be on the cation, the structure is most strongly influenced by the repulsion between the several adjacent fluorine anions. Complex ions are observed of the form K_2AnF_6 and K_3AnF_6 where An stands for the actinide ion which is tetravalent in the first case and pentavalent in the second.

Referring to Fig. 11 where the ionic radii for divalent, trivalent and tetravalent ions are plotted against the atomic number we see that the maximum coordination number for elements up to E108 would be 7 and probably a capped octahedron might be involved for the lighter members of this series of 6d transition elements, but the octahedral arrangement would be most likely. Apparently the trigonal prism (C_{3h}) or the trigonal anti-prism are less likely in a sense the trigonal anti-prism (C_{3v}) is a version of a hexagonal lattice with the stacking sequence being ABAB on alternate planes of fluorine.

For *d*-transition metals, six is the highest coordination number observed and these metals show a strong tendency to be octahedrally coordinated. The square planar arrangement is another common form. In as much as these compounds would not involve unfilled 5*f*-shells of the actinides

their bonding, it is by far more likely that the structural features of the elements E108–E110 would be similar to that encountered with platinum compounds and the elements of the 5*d* transition series.

SOLVATION OF IONIC SPECIES

Because of Prof. Mendeleev spent much of his professional life after elucidation of the Periodic Table working on aqueous solutions, it is appropriate to devote a little of this paper to the interaction of heavy and slightly charged ions with water.

In a previous paper, the Dirac–Slater Hamiltonian was modified by Liberman and Waber[37] to allow for the presence of a medium with a dielectric constant *D* greater than unity. Calculations using this modification were carried out for negative oxygen and sulphur ions as well as for sodium and

chloride ions. Waber and Anacker[38] did calculations on plus three and plus four ions of actinide elements. In these, it was found that the presence of the dielectric did not alter order of stability of the electronic configurations.

The energy associated with the induced alignment of water molecules near the central ion was also evaluated. This is illustrated in Fig. 12. Taken together, the lowering in energy from the aligned dipoles and the increased stability of the ion due to the influence of the dielectric medium, were reasonable. Typical values are shown in Table 3. Together they are somewhat larger than the thermodynamic heat of solvation of several trivalent ions as shown in Table 4.

Waber and Anacker[39] subsequently included the effect of the Debye–Hückel atmosphere into the Hamiltonian. They investigated certain cases where the Debye–Hückel theory does not lead to satisfactory results. The Debye–Hückel expressions arise as approximations of the Poisson–Boltzman equation

$$\nabla^2 V = -\frac{4\pi}{D} \sum_i n_i z_i \exp \left[\frac{-z_i V_i(r)}{kT} \right]$$

where n_i is the concentration of a given species, which describes the potential caused by a statistical

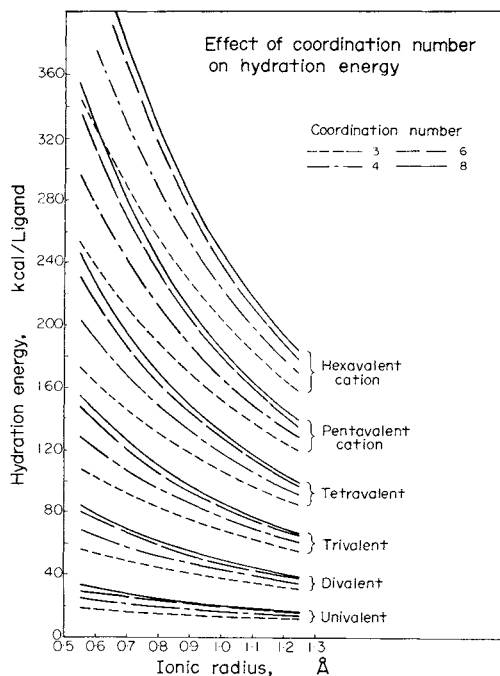


Fig. 12. Effect of the number n of water molecules coordinated to a central ion and the effect of the ionic radius on the dipole and induced dipole contribution to the solvation energy U per ligand (after Waber and Anacker[38]).

Table 3. Contributions to the heat of hydration for trivalent actinide ions in the general configuration $f^n f^q$ assuming octahedral coordination

	Dielectric effect ΔE_T		Dipole energy		
	Ry	kcal	T_1	nU	Total kcal
Uranium	1.9974	626.6	0.94	540	1166
Neptunium	1.9963	626.2	0.92	552	1178
Plutonium	1.9979*	626.8	0.90	564	1191
	1.9985	627.0			
Americium	1.9994	627.3	0.88	576	1203

*Based on $f^n s^1$ configurations.

Table 4. Thermodynamic heat of hydration

Ion	Method (I)	Method (II)
U^{+3}	801 kcal	811 kcal
Np^{+3}	807	820
Pu^{+3}	815.3	829
Am^{+3}	822	839
Cm^{+3}	830	847
Lanthanide ions [14]		
La^{+3}	792	
Lu^{+3}	887	

Private communication, J. Cleveland (1972).

distribution of counter-ions. Guggenheim [40] and subsequently LaMer *et al.* [41] attempted to solve this equation for 3:3 electrolytes. They found that even numerical procedures failed to give a convergent solution for $V(r)$.

Using modern computer, Waber and Anacker were able to obtain convergent solutions and computed activity coefficients. This is properly the subject for another time. However, discussion of this will be deferred and hence discussed as a separate paper.

In connection with the superheavy elements, one series of calculations was carried out on element E112. The results are summarized in Fig. 13. On the left hand side of each panel, the energy levels of the free ion are shown. The similar levels for the ions immersed in a medium with a dielectric constant are given on the right hand side. Here again one finds no change in the stability of the individual configurations. A steady change from $d^n s^2$ towards $d^n s^0$ is shown as the ionization increases. For this mercury-like element, if a plus four state could be induced, it would be the two s electrons which would be removed *after* the two holes were produced in the p -shell when the divalent cation $E112^{+2}$ was formed. A very interesting feature of this graph is how clearly it illustrates that the ions when immersed in a medium are significantly more stable than in vacuum.

Ionization and solvation of Element E 112

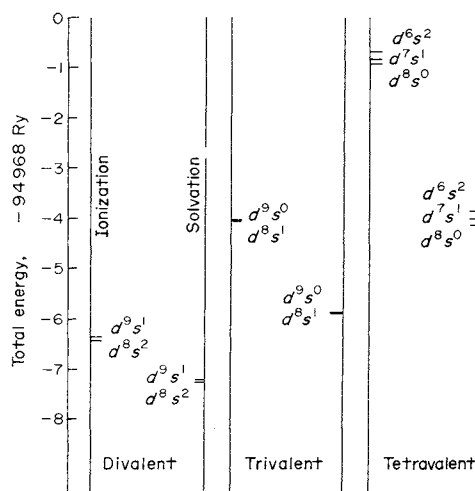


Fig. 13. Total energy values of ions of E112 and the reduction caused by a medium with a dielectric constant D equal to 80. Note that the dielectric causes no reordering of the energy levels.

SUMMARY

A quasi-molecular species may occur during bombardment of a target by highly accelerated heavy ions. The number of electrons removed \bar{q} has been discussed, as well as the deviation d of this number. Assuming \bar{q}/Z to be as large as 0.46, the electronic levels of the united atom have been correlated with the levels in the parent atomic species. Following the rules dictated by symmetry and the number of radial nodes in the orbitals some electrons will be promoted and other levels will be unoccupied. This will lead to the production of X-rays. The effect of the proton number on the energy levels for the iso-electronic set $E114^{+36}$ and $E122^{+44}$ have been shown on an extended form of the diabatic correlation diagram. The problem of detecting and identifying transitory nuclear or quasi-molecular species which might occur during

ionic bombardment have been reviewed and some of the limitations of using emitted X-rays are indicated.

On the other hand, some isotopes of the synthetic platinum-like elements may be stable. If that is the case, the chemists will have a rich field of endeavor. Some attention was given to rationalizing the extended Periodic Table during another lecture of this Conference. The orderly filling of the levels was discussed in terms of *jj* coupling.

The formation of positive as well as negative ions of the platinum-like element, E107–E110 was discussed. The special stability of $(7s\frac{1}{2})^2$ orbitals which is frequently referred to as the "lone pair effect" is explained by the relativistic treatment. The ease of forming holes in the d levels also suggests that covalent rather than ionic bonds will form.

Any discussion of the chemistry of new elements would not be complete without some reference to their aqueous ions. Since the Mendeleev Centennial in 1969, a basis for calculating the heat of solvation has been developed and tested. In one of the present lectures (p. 25), Nugent used his linearization scheme for estimating ionization potentials to take the important step of setting up formal electrode potentials. The missing ingredient in completing a Born–Haber cycle is the heat of vaporization of these elements, E108 to E112. While such data may be extrapolated from thermodynamic data an independent theoretical study of the solid element is feasible.

In short, it looks likely that much of the necessary quantum chemistry of superheavy elements will be ready in time to assist with the separation of such elements, should they prove to have reasonable half-lives. Then their place in the Periodic Table can be securely established by both physical and chemical studies.

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