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Are Elements 112, 114, and 118 Relatively Inert Gases?

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Several recent papers present estimates of physical and chemical properties of super-heavy elements based on combinations of periodic table trends and relativistic Hartree-Fock (DHF) calculations for the atoms. The appropriateness of relativistic orbitals for covalent bonding must also be considered before reliable conclusions can be reached, and we are studying that aspect. Initial results lead to the striking conclusion that elements 112 and 114, with closed s^2 and $p_{1/2}^2$ shells, respectively, are volatile and relatively inert, as 118 is also expected to be. Since long nuclear lifetimes have been predicted for elements near 114, there is particular interest in this region. Earlier publications[1] offer no such striking conclusion for 112, but Keller, et al.,[2] predict somewhat similar properties for 114 on the basis of rather different arguments.

In order to determine the effectiveness of a Dirac orbital for bonding in either a metal or a covalent compound, one may examine the angular function for each large component and its capacity to overlap the corresponding function on adjacent atoms. Alternatively, one may determine the appropriate functions for the very strong electric fields arising

in bonding situations. Bethe and Salpeter[3] show that for strong electric fields m_ℓ and m_s replace j and m as the good quantum numbers.

From the more detailed consideration of the angular functions,[4,5] one finds that relativistic s orbitals are appropriate for bonding. But a molecular orbital based on $p_{1/2}$ atomic orbitals is 1/3 σ-bonding and 2/3 π-antibonding on the basis of the large components. To obtain full σ-bonding character the combination $(1/3\ p_{1/2} + 2/3\ p_{3/2})$ must be taken.

While our studies of this question are continuing, it appears that the best simple approximation for chemical bonding with p orbitals is to adopt valence states with weighted average $(1/3\ p_{1/2} + 2/3\ p_{3/2})$ energies. Similarly for bonding with d orbitals the $(2/5\ d_{3/2} + 3/5\ d_{5/2})$ average energies are appropriate while for s electrons the relativistic orbital energies may be used directly. These energies are best taken from the calculations of Desclaux[6] since these are for LS configuration averages and are otherwise the most accurate available.

In Table 1 are given the promotion energies and the heats of sublimation (in ev) for the group 2 and 4 elements. The valence states are sp and p^2, respectively; data for germanium and gray tin are omitted since they have tetravalent structures. The sums in the last column represent bonding energies, i.e., energies to dissociate the crystal to atoms in their valence states.

For group 2 elements the bonding energy is 5-6 ev which is insufficient to promote atoms of 112 from the s^2 closed shell to the sp valence state. Similarly for group 4 elements the bonding energy is about 4 ev which is insufficient

Table 1

Energy Values in eV

	Promotion	Sublimation	Total
Zn	4.15	1.35	5.50
Cd	3.76	1.16	4.92
Hg	5.17	0.64	5.81
112	8.57	-	-
Sn	0.58	3.13	3.71
Pb	2.00	2.02	4.02
114	6.21	-	-

to promote atoms of 114 from the $p_{1/2}^2$ closed shell to the p^2 valence state. Thus I estimate that both 112 and 114 in elementary form will be gases or very volatile liquids bound by dispersion (London) forces only.

Such a simple argument cannot preclude the possibility of some very weak metallic properties in the liquid state. Indeed extrapolation from Zn and Cd on this basis could suggest the same "prediction" for mercury as for element 112. But the excess of promotion energy over expected bond energy is much greater for either 112 or 114 than for Hg, and Hg is, indeed, a volatile liquid; hence our primary conclusion seems not too uncertain.

For element 112 the configuration $d_{5/2}^5 s^2 p$ is lower than $d_{5/2}^6 sp$. The former is not a good bonding state, however, because the large s^2 closed shell will generate strong repulsive forces before the d orbitals are close enough to interact and because the $d_{5/2}$ orbitals are not good bonding orbitals in any case.

For element 118 the conventional promotion energy np^6 to $np^5(n+1)s$ is 8.8 ev which is not much less than Rn(9.2) or Xe(9.9). One can also consider a valence state $np_{3/2}^3(n+1)s$ in which only the s electrons would be expected to bond effectively. Then for 118 the promotion energy is only 4.89 ev, but this far exceeds the bonding expected for a single s electron which, by analogy to the alkali metals, is about 1 ev. Hence 118 should also be a gas or very volatile liquid.

Estimates of the stability of primarily covalent compounds can be made on a similar basis. One assumes that the bonding energy of the compound (from the atom in its valence state) for 112 is the same as Hg and that for 114 is the same as Pb. If we assume elements 112 and 114 boil at room temperature, a heat of vaporization of about 6 kcal (0.26 ev) should be added to the promotion energies in Table 1. Then 112 compounds will be less stable than the corresponding mercury compounds by 3.0_2 ev or 70 kcal/mole which is the difference in the energies to form atoms in their valence states. The corresponding difference of 114 from Pb is 2.4_5 ev or 56 kcal/mole. Addition of 70 kcal to the free energies of formation of mercury compounds[7] yields positive values (indicating instability) for most compounds including the neutral oxide, chloride, and bromide, although the $MCl_4^=$ and $MBr_4^=$ ions remain stable. There is no numerical value for HgF_2, but there is little doubt that the fluoride of 112 will be stable.

Earlier estimates[1] have not suggested any such extreme volatility and chemical inertness for element 112 as is here indicated.

The corresponding calculation for compounds of 114 yield positive free energies of formation for the oxide (+11) and the iodide (+15) but a small negative value for the bromide (-6). The chloride and fluoride are expected to be stable; however, with increasing ionic character the calculation on a covalent basis becomes less appropriate. Although our results

indicate 114 to be somewhat more volatile and more noble than those of \Keller, et al.,[2] the difference is not large.

These properties of great volatility and ease of reduction to the element would appear to provide better separation methods than procedures based on uncertain quantitative similarities in solution chemistry of 112 to mercury and 114 to lead.

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