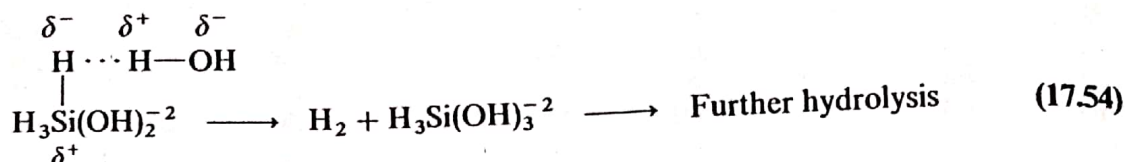


reacting with a positive hydrogen from water:



The lack of reactivity of germane and stannane could result from the absence of a $M^{\delta+} - H^{\delta-}$ dipole of sufficient magnitude to induce reaction, i.e., if the electronegativities of Ge and Sn are closer to that of hydrogen than that of Si. The behavior of the reactions of the triphenyl derivatives with lithium alkyls supports a similar interpretation: When bonded to a more electronegative carbon or germanium atom,⁵¹ a hydrogen atom will be more acidic than when bonded to a less electronegative silicon or tin atom.⁵¹

Finally, Allred and Rochow examined the bond energies of the Group IVA halides (see Table 17.5). They noted that although the homopolar bond energies of Si—Si and Ge—Ge are almost identical (188 and 186 kJ mol⁻¹), Ge—X bonds are from 21 to 113 kJ mol⁻¹ weaker than Si—X bonds. This difference in energy can be assigned to differences in electronegativity *only if germanium has a higher electronegativity than silicon and when bonded to electronegative halogens yields smaller ionic resonance energies*. By a series of Pauling-type calculations⁵² they obtained the following electronegativities for the Group IVA elements (all sp^3 hybrids): C = 2.60 (assumed), Si = 1.91, Ge = 2.00, Sn = 1.94, Pb = 2.23.

Two of the Allred-Rochow experimental values⁵³ (Ge and Pb) for the electronegativities deserve special comment. That the electronegativity of germanium is greater than that of either silicon or tin is supported by three electronegativity scales: the Allred-Rochow electrostatic scale, the Sanderson relative compactness scale, and the Mulliken-Jaffé ionization energy scale.⁵⁴ The former two are based on size and reveal the results of the contraction across the first transition series. The latter, based on ionization and electron affinity energies, reflects the increased ionization energy resulting from poor shielding by d electrons. They are thus in essential agreement over the nature of the increase in electronegativity for germanium. This coupled with the experimental evidence given above makes most inorganic chemists accept the higher value for germanium.

The electronegativity of lead is still a matter of considerable disagreement. On all counts the data available for calculations for lead are poor. Exact values for its radius, effective atomic number, ionization energy, electron affinity, and bond energies are much more difficult to obtain than for the lighter elements. On the basis of other work, Allred and Rochow suggested an even higher value than that derived from bond energies, 2.45!

⁵¹ The relative electronegativities of Ge and Sn vary somewhat but are obviously close to hydrogen and greater than silicon. Substituent effects could be responsible for these small variations.

⁵² The interested reader is referred to the original paper for details of the calculations.

⁵³ These are the values obtained from bond energies and other experimental work described above and should not be confused with the Allred-Rochow electrostatic values. See p. 149.

⁵⁴ Although this scale has the soundest theoretical basis, in the present instance it is of limited usefulness since all of these elements except carbon utilize some (unknown) amount of d character and the d orbitals have low (unknown) electronegativities. The values for the sp^3 hybrids are all somewhat high therefore.

Many workers, including Drago,⁵⁵ could not accept such a high value (yet note that even the "conservative" Pauling scale gave Au a value of 2.4, 0.5 unit higher than Ag, and both Hg and Tl were given values higher than their lighter congeners). In support of a higher value for lead (not necessarily as high as 2.45) it may be pointed out that both the ionization energy and electron affinity (see Table 2.5) of lead are relatively high as a result of the addition of 14 poorly shielded protons across the lanthanide series.⁵⁶

The controversy has not as yet been completely resolved. It is interesting to note (and to oversimplify somewhat) that Drago assumed the constancy of electronegativity (Si—Pb), the concomitant constancy of ionic bonding, and hence was forced to the conclusion that something was peculiar with the overlap and/or repulsions in the bonds of Ge and Pb. On the other hand, Allred and Rochow assumed that all of the bonds were more or less normal in behavior as far as the covalent contribution was concerned—hence differences in bonding reflected differences in ionic character and higher electronegativities for Ge and Pb.⁵⁷ By extension, this would ascribe the "inert pair effect" to weak bonds in the heavy metals because they are not stabilized by ionic character. It is interesting to note that both points of view agree on one point, an empirical observation: Those elements such as Ga, Ge, and As that follow the first transition series and those elements such as Tl, Pb, and Bi that follow the first lanthanide or inner transition series are affected by the increased effective nuclear charge and exhibit unusual properties. When exhibited by the fourth-row elements it may be referred to as a "reluctance to exhibit the maximum oxidation state (for As, Se, and Br)," and when shown by the sixth-row elements it may be termed the "inert pair effect." In both cases it probably rests ultimately on the effects of unshielded nuclear charge.⁵⁸

This behavior has been generalized as follows. Those elements that follow the first filling of a given type of sublevel (*p*, *d*, *f*, etc.) will exhibit a lowered tendency to form stable compounds in their highest oxidation states.⁵⁹ This correlates the behavior of the post-lanthanide (first filling of *f* levels) elements (Hf to Rn) and the postscandide (first filling of *d* levels) elements (Ga to Kr). In addition, more subtle effects can also be found: Both sodium and magnesium form less stable compounds than would be expected on the basis of the behavior of their lighter (Li, Be) and heavier (K, Ca) congeners.⁶⁰ These elements are those that follow immediately after the first filling of a set of *p* orbitals (Ne), and the same effects of incomplete shielding (though less pronounced to be sure) presumably are operative

⁵⁵ R. S. Drago, *J. Inorg. Nucl. Chem.*, **1960**, *15*, 237. This was followed by a rebuttal from Allred and Rochow, and the debate has continued. The interested reader is urged to study this controversy as an excellent example of a situation in which intelligent and knowledgeable workers can take the same data and interpret them in diametrically opposite ways! See A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1960**, *20*, 167; R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.*, **1965**, *3*, 62.

⁵⁶ Unfortunately the spectroscopic data necessary to calculate promotion energies and valence state ionization energies and electron affinities are not available, so it is impossible to provide a Mulliken-Jaffé electronegativity.

⁵⁷ Both sets of authors have done a considerably better job of arguing their points of view than can possibly be represented in the space available here.

⁵⁸ For a discussion of these problems, see W. E. Dasent, "Nonexistent Compounds," Dekker, New York, **1965**, Chapters 5 and 6. For a discussion of the use of *d* orbitals in these elements, see D. S. Urch, *J. Inorg. Nucl. Chem.*, **1963**, *25*, 771.

⁵⁹ J. E. Huheey and C. L. Huheey, *J. Chem. Educ.*, **1972**, *49*, 227.

⁶⁰ R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **1970**, *32*, 777.

here as well as in the postlanthanide and postscandide elements. This principle has been used to predict some of the chemical properties of the superheavy transactinide elements.⁵⁹

"Anomalous" ionization energies and electron affinities

Many introductory chemistry books give simple rules for remembering the periodic changes of ionization energies and electron affinities. The rules usually follow some modification of "Ionization energies and electron affinities increase as one moves to the right in the periodic chart; they decrease as one moves from top to bottom." These generalizations, as well as the shielding rules that account for the atomic behavior, were discussed in Chapter 2, along with some of the exceptions. Unfortunately for simplicity, the exceptions are somewhat more numerous than is generally realized. Many of the problems discussed in the preceding sections result from these "exceptions."

The horizontal behavior of atoms follows the general rule with good regularity as might be expected from adding a single proton at a time with expected monotonic changes in properties. We have already seen the exception of the inversion of the ionization potentials of the VA and VIA groups related to the stability associated with half-filled subshells. A similar inversion of electron affinities takes place, for the same reason, between groups IVA and VA.

The vertical exceptions to the generalizations are much more widespread: If we count every time that a heavier element has a higher ionization potential or higher electron affinity than its next lighter congener, we find that about one-third of the elements show "electron affinity anomalies"⁶¹ and a somewhat higher fraction of the elements show "ionization energy anomalies." With such a high fraction of exceptions, one wonders why the rules were formulated as they were originally. The answer seems to lie in the lack of data available until recently; most of the good data were for familiar elements, such as the alkali metals and the halogens. For these main-group elements, with the exception of the lower electron affinity of fluorine resulting from electron-electron repulsion (and paralleled by oxygen and nitrogen), the rules work fairly well; however, the poorer shielding *d* and *f* electrons upset the simple picture. For the transition metals, higher ionization energies with increasing atomic number in a group are the *rule*, not the exception. As we have seen in the preceding discussion, this carries over somewhat into the posttransition elements, causing some of the problems associated with families IIIA and IVA.

The increased ionization energies of the heavier transition metals should not be unexpected by anyone who has had a modicum of laboratory experience with any of these elements. Although none of the coinage metals is very reactive, gold has a well-deserved reputation for being less reactive than copper or silver;⁶² iron, cobalt, and nickel rust and corrode, but osmium, iridium, and platinum are noble and unreactive and therefore are used in jewelry; platinum wires are the material of choice for flame tests without contamination; and one generates hydrogen with zinc and simple acids, not with mercury.

⁶¹ E. C. M. Chen and W. E. Wentworth (*J. Chem. Educ.*, 1975, 52, 486) have reviewed the experimental values of atomic electron affinities and plotted them periodically.

⁶² The legend of *aqua regia* seems to persist even in the absence of student contact with this powerful elixir.