

Periodicity

The most fascinating aspect of inorganic chemistry as well as its most difficult problem is the diversity of reactions and structures encountered in the chemistry of somewhat over one hundred elements. The challenge is to be able to treat adequately the chemistry of boranes and noble gas fluorides and ferrocene and lanthanum compounds without developing a separate set of rules and theory for each element. The tool that has kept the inorganic chemist from throwing up his hands in despair is the periodic table, now slightly over one hundred years old.¹ It is of such overwhelming importance in the correlation of the properties of the elements that entire books have been written on this theme.² It is considered so essential that no general chemistry textbook would be complete without a discussion of the trends summed up in Chapter 2 (pp. 38–50). Unfortunately the impression is often given that all of the periodic properties vary smoothly.

Fundamental trends

The fundamental trends of the periodic chart have been discussed in Chapter 2. They may be summarized as follows. Within a family there are increases in size and decreases in ionization energy, electron affinity, electronegativity, etc. Increasing the atomic number across a given period results in concomitant increases in ionization energy, electron affinity, and electronegativity but a decrease in size. The change in effective atomic number within a period is reasonably smooth, but the various periods differ in length (8, 18, and 32 elements). The properties of an element will depend upon whether it follows an 8, 18, or 32 sequence. One of the best known examples is the similarity in properties of

¹ Periodic classifications of the elements by Dmitri Mendeleev and by Lothar Meyer appeared in 1869. For a centennial-celebrating discussion of the periodic table, see J. W. van Spronsen, "The Periodic System of Chemical Elements," Elsevier, Amsterdam, 1969.

² R. Rich, "Periodic Correlations," Benjamin, New York, 1965; R. T. Sanderson, "Chemical Periodicity," Van Nostrand-Reinhold, New York, 1960. The latter book was rewritten but kept the periodicity theme and appeared under the title "Inorganic Chemistry" in 1967.

hafnium, tantalum, tungsten, and rhenium to those of zirconium, niobium, molybdenum, and technetium, respectively, as a result of the lanthanide contraction (see Chapter 12). Similar effects follow the filling of the d levels (very rarely referred to as the "scandide" contraction). A second factor tending to affect the regularity of properties is the absence of d orbitals in the elements lighter than sodium. This results in a discontinuity of properties from the second-row elements, Li–F, to the heavier congeners.

FIRST- AND SECOND-ROW ANOMALIES

In many ways the first ten elements differ considerably from the remaining 90%. Hydrogen is a classic example—it belongs neither with the alkali metals nor with the halogens although it has some properties in common with both. Thus it has a +1 oxidation state in common with the alkali metals, but the bare H^+ has no chemical existence³ and hydrogen tends to form covalent bonds that have properties more closely resembling those of carbon than those of the alkali metals. With the halogens it shares the tendency to form a –1 oxidation state, even to the extent of forming the hydride ion, H^- ; however, the latter is a curious chemical species. In contrast to the proton which was anomalous because of its vanishingly small size, the hydride ion is unusually large. It is larger than any of the halide ions except iodide!⁴ The source of this apparent paradox lies in the lack of control of a single nuclear proton over two mutually repelling electrons. Since the hydride ion is large and very polarizable it certainly does not extend the trend of I^- through F^- of decreasing size and increasing basicity and hardness.

The elements of the second row also differ from their heavier congeners. Lithium is anomalous among the alkali metals and resembles magnesium more than its congeners. In turn, in Group IIA beryllium is more closely akin to aluminum than to the other alkaline earths. The source of this effect is discussed below. We have already seen that fluorine has been termed a superhalogen on the basis of its differences from the remainder of Group VIIA.

One simple difference that the elements Li to F have with respect to their heavier congeners is in electron-attracting power. Thus fluorine is much more reactive than chlorine, bromine, or iodine; lithium is less reactive than its congeners.⁵ The most electronegative and smallest element of each family will be those of the second row.

The great polarizing power of the Li^+ cation was commented upon in Chapter 3. As a result of its small size and higher electronegativity this ion destabilizes salts that

³ Those who disapprove of writing H_3O^+ often point out that the hydration number of the H^+ is uncertain and "all cations are hydrated in solution." To treat H^+ (rather than H_3O^+) as a cation similar to Na^+ , for example, is to equate nuclear particles with atoms, a discrepancy by a factor of about 10^5 .

⁴ Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, 1960, p. 514, has provided an estimate of 208 pm for the hydride ion compared to 216 pm for I^- . To be sure, the existence of an unpolarized hydride ion is even less likely than an unpolarized anion of some other kind, but insofar as ionic radii have meaning this would be the best estimate of the size of a free hydride ion.

⁵ The inherent unreactivity of lithium is offset in aqueous solution by the exothermic hydration of the very small Li^+ ion. Nevertheless, in general, lithium is a less reactive metal than Na, K, Rb, or Cs.

are stable for the remaining alkali metals:



In contrast, for the large polarizable hydride ion which can bond more strongly by a covalent bond the lithium compound is the *most* stable:



The diagonal relationship

It was mentioned previously that a strong resemblance obtained between Li and Mg, Be and Al, C and P, and other "diagonal elements," and it was pointed out that this could be related to a size-charge phenomenon (see p. 130). Some examples of these resemblances are as follows:

Lithium-magnesium. There is a large series of lithium alkyls and lithium aryls which are useful in organic chemistry in much the same way as the magnesium Grignard reagents. Unlike Na, K, Rb, or Cs, but like Mg, lithium reacts directly with nitrogen to form a nitride:



Finally, the solubility of several lithium compounds more nearly resembles those of the corresponding magnesium salts than of other alkali metal salts.

Beryllium-aluminum. These two elements resemble each other in several ways. The oxidation *emfs* of the elements are similar ($\mathcal{E}_{\text{Be}}^0 = 1.85$; $\mathcal{E}_{\text{Al}}^0 = 1.66$), and although reaction with acid is thermodynamically favored, it is rather slow, especially if the surface is protected by the oxide. The similarity of the ionic potential (see p. 130) for the ions is remarkable ($\text{Be}^{+2} = 6.45$, $\text{Al}^{+3} = 6.00$) and results in similar polarizing power and of the cations. For example, the carbonates are unstable, the hydroxides dissolve readily in excess base, and the Lewis acidities of the halides are comparable.

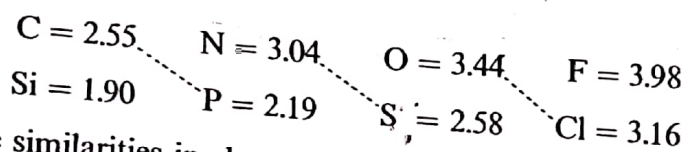
Boron-silicon. Boron differs from aluminum in showing almost no metallic properties and its resemblance to silicon is greater. Both boron and silicon form volatile, very reactive hydrides; the hydride of aluminum is a polymeric solid. The halides (except BF_3) hydrolyze to form boric acid and silicic acid. The oxygen chemistry of the borates and silicates also has certain resemblances.

Table 17.1 Maximum coordination numbers of the nonmetals as shown by the fluorides

CF ₄	NF ₃ ^a	OF ₂ ^a	FF(F ₃ ⁻)
SiF ₆ ⁻²	PF ₆ ⁻	SF ₆	ClF ₅ ^a
			⋮
			IF ₇ (IF ₈ ⁻)

^a N, O, and other elements can achieve higher coordination in onium salts, e.g., NH₄⁺.

Carbon-phosphorus, nitrogen-sulfur, and oxygen-chlorine. All metallic properties have been lost in these elements, and so charge-to-size ratios have little meaning. However, the same effects appear in the electronegativities of these elements, which show a strong diagonal effect:⁶



The similarities in electronegativities are not so close as those of the ionic potential for Be⁺² and Al⁺³. The heavier element in the diagonal pair always has a lower electronegativity, but the effect is still noticeable. Thus, when considering elements that resemble carbon, phosphorus is as good a choice as silicon, and the resemblance is sufficient to establish a base from which notable *differences* can be formulated.

THE USE OF *d* ORBITALS BY NONMETALS

It is an obvious fact that the elements Li to F are restricted to the set of *s* and *p* orbitals, but their heavier congeners such as Na to Cl can use 3*s*, 3*p*, and 3*d* orbitals. This provides extra opportunities for bonding in the heavier elements that their light congeners do not enjoy. The extent to which these elements use valence shell *d* orbitals is a matter of some controversy. Some of the experimental evidence will be discussed first, followed by theoretical interpretations.

Experimental evidence for σ bonds involving *d* orbitals

It is a fact that the second-row elements, Li to F, show a maximum covalence of 4,⁷ corresponding to a maximum hybridization of *sp*³. In contrast, third-row and heavier elements show 5, 6, and 7 coordination (Table 17.1) consistent with use of *d* orbitals.

⁶ These values are Pauling thermochemical electronegativities rather than those based on ionization energy-electron affinity. This choice of empirical values was made to obviate the necessity to choose (arbitrarily) the proper hybridization.

⁷ In the metallic state lithium and beryllium have coordination numbers greater than 4, as does elemental boron in icosahedral structures. In each of these examples multicenter bonding occurs and the concept of fixed bonds is not applicable.

A second factor
require the assen-
ordinar-

A second factor which may affect the coordination number and which does not require the assumption that *d* orbitals participate is size. One would expect that the coordination number would increase upon progressing down the chart, and indeed it does. Thus the number of σ bonds a nonmetal forms may be determined as much by the number of substituents that can fit as by the number of orbitals available.

Experimental evidence for π bonding;
the phosphorus-oxygen bond in phosphoryl compounds

In the case of π bonding we again find the old problem of detecting the existence of a bond. We can infer the presence of a σ bond when we find two elements at distances considerably shorter than the sum of their van der Waals radii. The detection of a π bond depends on more subtle criteria: shortening or strengthening of a bond, stabilization of a charge distribution, etc., experimental data which may be equivocal.

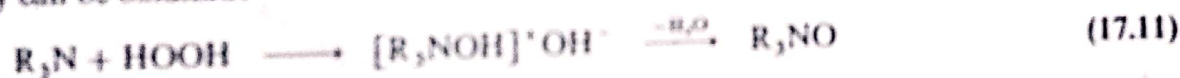
One example of the apparent existence of π bonding is in phosphine oxides. Most tertiary phosphines are unstable relative to oxidation to the phosphine oxide:



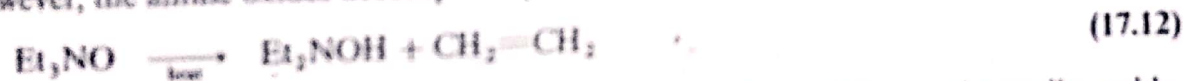
This reaction takes place so readily that aliphatic phosphines must be protected from atmospheric oxygen. The triarylphosphines are more stable in this regard but still can be oxidized readily:



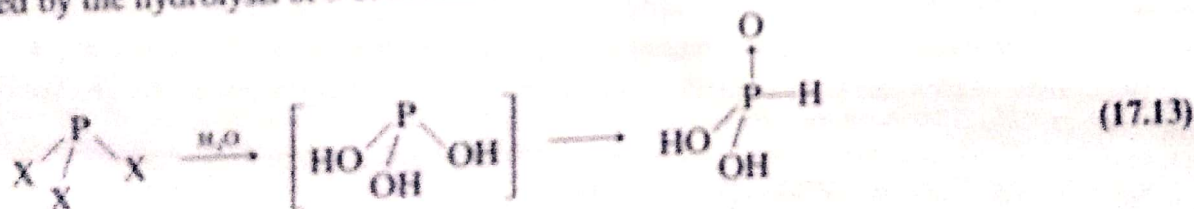
In contrast, aliphatic amines do not have to be protected from the atmosphere although they can be oxidized:



However, the amine oxides decompose upon heating:



a reaction completely unknown for the phosphine oxides, which are thermally stable. In fact, it has been said that "tertiary phosphine oxides have the reputation of being the most stable chemical structures in the family of organophosphorus compounds."⁴ They are not reduced even by heating with metallic sodium. The tendency of phosphorus to form such P-O or P=O linkages is one of the driving forces of phosphorus chemistry and may be used to rationalize and predict reactions and structures. For example, the lower phosphorus acids exist in the 4-coordinate structures even though they are prepared by the hydrolysis of 3-coordinate halides:



⁴ J. R. Van Wazer, "Phosphorus and Its Compounds," Wiley (Interscience), New York, 1958, Vol. I, p. 287.