

Chapter 6

Periodic Properties of the Elements

Invoking the orbital model of a many-electron atom, we reshape Lewis's intuitive ideas of atomic valence into a quantum mechanical theory—an idealized picture of quasi-independent electrons moving in hydrogen-like Coulomb potentials, occupying hierarchical orbitals according to the Pauli exclusion principle. The pairing of electron spins, a consequence of exclusion, proves to be a key factor in building up the periodic table.

The exercises here fall into three broad groupings, adhering mostly to the sequence followed in the chapter: (1) the approximations of the orbital model and the interwoven concepts of penetration, shielding, electron-electron repulsion, and effective nuclear charge (Section 6-1); (2) the Aufbau principle and the buildup of electron configurations in complex atoms, with special attention given to anomalous systems (Section 6-2); and (3) a rationalization of chemical periodicity (Section 6-3).

Tables C-8 and C-10 in PoC (beginning on pages A68 and A76, respectively) offer ready compilations of electronic configurations and properties, helpful especially for readers who wish to confirm or criticize qualitative predictions based on the orbital model.

The first 16 exercises address general questions concerning the orbital approximation (pages 178–181), the exclusion principle (pages 181–182), penetration and shielding (pages 182–186), electron-electron repulsion and Hund's rule (pages 186–191), and peculiarities of the d configurations (pages 195–198). See also pages R6.1–R6.3 and Examples 6-1 through 6-3.

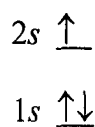
1. In the hydrogen atom, a single electron moves in the attractive Coulomb potential of a single nucleus. The wave functions thus derived (the orbitals) are exact solutions of the Schrödinger equation. With two electrons or more, however, the $1/r$ symmetry of the electrostatic interaction is destroyed by repulsion between the negative particles. The single-electron orbitals appropriate for hydrogen are no longer valid for helium and beyond. The many-body problem (electrons plus nucleus) cannot be solved exactly.

(a) As an approximation, we replace the complicated moment-to-moment, point-by-point pattern of electron-electron repulsion by an average potential constructed for every electron in turn. One at a time, we imagine each electron to move about the nucleus as if it were all alone in a hydrogen-like environment. Repulsion from the other electrons is treated as coming from a lone centrosymmetric source, and solutions to the modified **Schrödinger** equation are, once again, single-electron orbitals similar to those obtained for hydrogen.

(b) Regard the notion of orbitals as a working model for the structure of a many-electron atom, subject to the assumptions and approximations made above. Whether or not an electron actually occupies its assigned region will depend on the smoothed-out picture of interelectronic repulsion that we first use to devise the orbital (a purely mathematical construct). Where the model does prove justified, the electrons should appear—with probability proportional to ψ^2 —in the regions prescribed by their respective orbitals ψ .

(c) Unusually strong electron-electron repulsion, particularly in heavy atoms, will compromise the orbital model. The *correlation* of electron motion, whereby electron 1 seems to “go out of its way” to avoid electron 2, also degrades the averaged $1/r$ approximation.

2. The notation $1s^2 2s^1$, on its face, asserts that the orbital model of atomic structure—an idealization—has been adopted to describe the atom. Each of the three electrons here is considered to move in its own potential and its own orbital, influenced in a general way by all the other electrons at once. The one-electron orbitals, analogous to those in hydrogen, are occupied as $1s^2 2s^1$ in accordance with the **Pauli** exclusion principle:



3. Electrons in the $1s$ orbital reside, on the average, closer to the nucleus than do electrons in the $2s$ orbital. As a result, either of the two $1s$ electrons in lithium is strongly attracted by nearly the full positive charge of a bare nucleus ($Z = 3$).

The $2s$ electron, pushed farther out by the intervening $1s$ electrons, interacts with a nucleus already partially shielded (or screened) by a core configuration with a nominal charge of -2 . The nucleus therefore appears to offer the valence electron a charge not of $+3$, but rather something closer to $+1$. In turn, the occasional penetration of the $2s$ electron also reduces the effective nuclear charge acting on the $1s$ electrons—to a value somewhat less than the bare-nucleus maximum of $+3$.

4. The term *penetration* describes the extent to which an electron spends time near the nucleus. The closer it gets, the stronger is the attraction.

Shielding, a consequence of penetration, is the effect that a “penetrating” electron has on some other electron more distant from the nucleus. The far-off electron responds to a nucleus partially screened by negative charge distributed closer to the nucleus. The

effective positive charge of the nucleus (which causes an attraction) is diminished by the countervailing negative charge of the more penetrating electrons (which causes a repulsion).

In reality, there is only a complicated web of electron-nucleus attractions and electron-electron repulsions. The simplifying picture of penetration and shielding condenses these interactions into an *effective nuclear charge*,

$$Z_{\text{eff}} = Z - S$$

in which the positive charge of the bare nucleus (Z) is reduced by a certain shielding factor S . The shielding factor is different for different values of n and ℓ , reflecting variations in the size, shape, and probability distribution of the orbitals.

See pages 182-1 86 in *PoC* and related discussion in the three preceding exercises.

5. Each electron in lithium interacts with a positive nuclear charge no greater than +3, the atomic number Z of the atom. Within the $1s$ orbital, however, one electron may screen the other by up to one full unit of negative charge, thus reducing the *effective* nuclear charge from +3 to +2. The expected range for Z_{eff} is then

$$2 \leq Z_{\text{eff}} \leq 3 \quad (1s)$$

for the two core electrons in Li. Theoretical calculations typically yield the value $Z_{\text{eff}} = 2.7$.

Outside the $1s$ orbital, the lone $2s$ electron is now subject to the screening of the two core electrons. The maximum screening effect is 2 units, which, if realized, would reduce the nuclear charge from $Z = 3$ to $Z = 1$:

$$1 \leq Z_{\text{eff}} \leq 3 \quad (2s)$$

The screening is nearly complete. A more detailed calculation shows that $Z_{\text{eff}} = 1.3$.

See pages 182-1 86 and 203-205 in *PoC*.

6. A second valence electron—the fourth electron overall—must be accommodated in beryllium. See, in particular, page 204 in *PoC*.

(a) Four electrons are distributed over the first two orbitals in Be, producing the configuration $1s^2 2s^2$.

(b) For the $1s$ electrons, the expected range is

$$3 \leq Z_{\text{eff}} \leq 4 \quad (1s)$$

The upper bound is limited by the atomic number, $Z = 4$. The lower bound assumes that one $1s$ electron screens the other by its full unit of negative charge (to yield $Z_{\text{eff}} = Z - 1$).

For the $2s$ electrons, the upper bound is again equal to the atomic number: $Z = 4$.

The lower bound, strictly speaking, is 1, as would arise if one $2s$ electron could screen the other completely (to yield $Z_{\text{eff}} = Z - 2 - 1$). More reasonable, though, is to estimate a value nearer $Z_{\text{eff}} = 2$, since the $2s$ electrons both penetrate to the same extent and consequently fail to screen each other significantly. The valence electrons would then interact with a nuclear charge effectively reduced by 2 units from its full value:

$$2 \leq Z_{\text{eff}} \leq 4 \quad (2s)$$

Theoretical calculations of Z_{eff} for the $1s$ and $2s$ orbitals in Be yield 3.7 and 1.9, respectively. Figure 6-11 in *PoC* (page 205) provides a graphical summary.

(c) Effective nuclear charges in Li are uniformly smaller: $Z_{\text{eff}}(1s) = 2.7$ and $Z_{\text{eff}}(2s) = 1.3$. See the preceding exercise for further discussion.

7. For a view in pictures, see the diagrams on page 204 of *PoC*. In lithium, one valence electron interacts with a three-proton nucleus screened by two core electrons—as if the attraction were to a nucleus with an effective charge of approximately +1:

$$Z_{\text{eff}} \approx Z - 2 = 3 - 2 = 1$$

In beryllium, two valence electrons interact with a *four*-proton nucleus also screened by two core electrons, so here the effective nuclear charge is approximately +2:

$$Z_{\text{eff}} \approx Z - 2 = 4 - 2 = 2$$

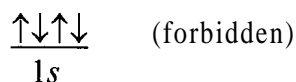
Attracted by a larger effective positive charge, the ionizable $2s$ electron in Be is therefore bound more tightly than the comparable $2s$ electron in Li. Beryllium has the higher ionization energy, as confirmed by Figure 6-16 in *PoC*. Its electron is harder to remove.

8. The Pauli exclusion principle asserts that no two electrons may occupy the same quantum state. They cannot be in the same place at the same time with the same spin.

For systems described by the orbital model, the exclusion principle thus restricts the occupancy of all orbitals to two electrons or fewer. Since n , ℓ , m_ℓ and m_s must assume a unique set of values for each electron, any two electrons sharing the same spatial quantum numbers (n , ℓ , m_ℓ) must have opposite spin components ($m_s = \pm\frac{1}{2}$).

9. The Pauli exclusion principle is a true law of nature—never violated, we think. Both of the proposed configurations are absolutely forbidden, as explained below.

(a) If the configuration

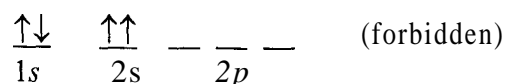


were to exist, then four electrons would occupy the same $1s$ orbital. There would be two sets of duplicate quantum numbers:

n	ℓ	m_ℓ	m_s
1	0	0	$\frac{1}{2}$
1	0	0	$-\frac{1}{2}$
1	0	0	$\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

To prevent such violations, the exclusion principle permits only two electrons to occupy a single spatial orbital: one with spin up ($m_s = \frac{1}{2}$) and one with spin down ($m_s = -\frac{1}{2}$).

(b) The impossible configuration



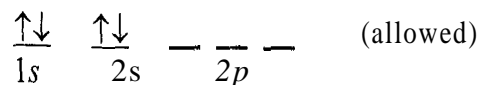
produces duplicate quantum numbers in the 2s orbital:

n	ℓ	m_ℓ	m_s
2	0	0	$\frac{1}{2}$
2	0	0	$\frac{1}{2}$

By contrast, the allowed configuration

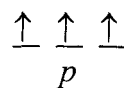
n	ℓ	m_ℓ	m_s
2	0	0	$\frac{1}{2}$
2	0	0	$-\frac{1}{2}$

ensures that the spins are paired:



See pages 181-182 of *PoC* and also Example 6-2.

10. Hund's rule (*PoC*, pages 188-191) deals with the probable distribution of electrons over a set of degenerate magnetic sublevels, as in a p^3 configuration:



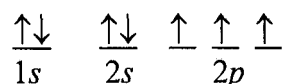
The rule, applicable to ground states only, asserts that an atom will usually maximize the number of unpaired electrons with parallel spins. Pairing occurs only after each spatial

orbital in a subshell is occupied by a single electron, its spin pointing in the same direction as all the others. Arranged in this way, the electrons involved suffer the least electrostatic repulsion. They tend to spend less time in the same region of space.

Other distributions are not strictly forbidden, but the one predicted by Hund's rule is most likely to occur.

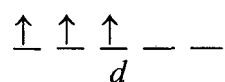
11. Hund's rule states that electrons tend to fill degenerate orbitals one sublevel at a time, maintaining parallel spins wherever possible. Placing one electron in each of two equivalent orbitals will yield a lower energy than pairing two electrons in the same orbital (where electron-electron repulsion would increase the total energy). Likewise, keeping the spins parallel helps to minimize unfavorable electron-electron encounters. The alignment of spin forces electrons to avoid each other, as demanded by the Pauli exclusion principle.

Configuration (b), the only one to have its three p electrons in separate orbitals with parallel spins, is the ground state predicted by Hund's rule:



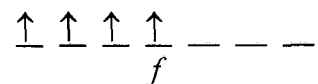
The other two configurations, although not absolutely forbidden, have higher energies and are less likely to occur. See pages 188-191 and Example 6-2 in *PoC*.

12. Configuration (c) is lowest in energy:

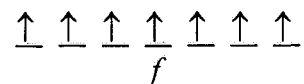


Each of the occupied sublevels contains only one electron, and all of the spins are parallel.

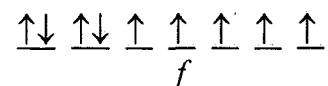
13. The most favorable configuration will contain four unpaired (and parallel) electrons, thus making the f^4 ground state paramagnetic:



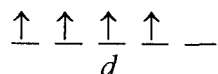
14. First, seven electrons enter the seven orbitals one at a time, avoiding pairing:



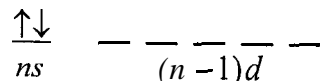
The two remaining electrons then double up to leave five electrons unpaired in an f^9 configuration:



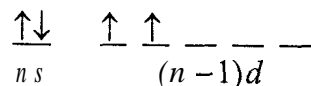
15. The four electrons fill the d orbitals one at a time, maintaining parallel spins in a paramagnetic d^4 configuration:



16. Under such circumstances, common among the transition metals, the s orbital is usually filled before the d orbitals. Two electrons first go into the ns level,



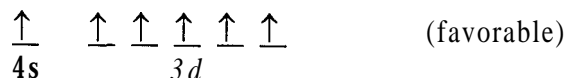
and the remaining electrons go into the $(n-1)d$ levels according to Hund's rule:



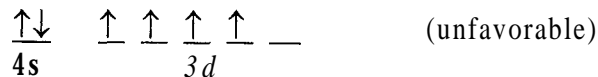
The four-electron configuration is thus $ns^2(n-1)d^2$, with two unpaired electrons—rather than $(n-1)d^4$, with four. See *PoC*, pages 195-197.

From the general to the specific... we go on to analyze the electron configurations of atoms and ions ranging over the whole periodic table. See Section 6-2 and also Examples 6-3 and 6-4.

17. The $4s^13d^5$ configuration

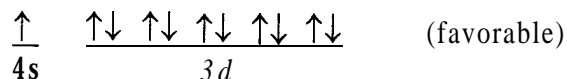


has a half-filled d subshell and consequently is lower in energy than $4s^23d^4$:

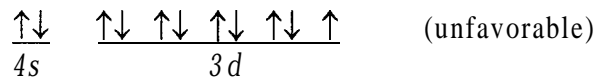


Electron-electron repulsion is less in the d^5 arrangement (the ground state of a chromium atom). See *PoC*, pages 197-198.

18. Here the $4s^13d^{10}$ configuration

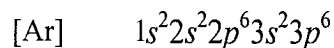


is preferred over $4s^23d^9$:



The completed d subshell in $4s^1 3d^{10}$ confers special stability on the electronic structure.

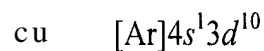
19. Chromium ($Z = 24$) has six valence electrons to distribute outside its 18-electron argonlike core. With the core configuration filled through $3p$,



the next available orbitals are the $4s$ and $3d$. The configuration of lowest energy, favored by a half-filled d subshell, is $4s^1 3d^5$:



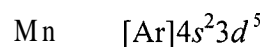
In copper ($Z = 29$) there are 11 valence electrons to distribute over the $4s$ and $3d$ orbitals. The preferred configuration, $4s^1 3d^{10}$, offers a completely filled d subshell:



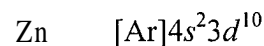
See Exercises 17 and 18, as well as pages 195-198 in *PoC*.

20. Refer back to Exercises 17 through 19 for a treatment of ground-state configurations in Cr and Cu, mentioned below.

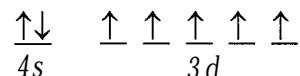
(a) Manganese ($Z = 25$) has one more electron than chromium, for which the valence configuration is $4s^1 3d^5$. The normal building-up sequence resumes with a return to the $4s$ subshell, producing a $4s^2 3d^5$ configuration in Mn:



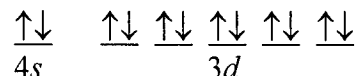
Similarly, zinc ($Z = 30$) adds one electron to the $4s^1 3d^{10}$ configuration of copper. The 12th valence electron goes into the vacancy in the $4s$ orbital, thereby closing the first series of transition metals with a $4s^2 3d^{10}$ configuration:



(b) Mn has five unpaired electrons, consistent with Hund's rule:



Zn, with a filled d subshell, has none:



21. See Section 6-2 in *PoC* for an atom-by-atom analysis of the Aufbau process.

(a) These elements, all belonging to the second row, fill their $1s$, $2s$, and $2p$ orbitals according to the normal building-up sequence:

$$1s < 2s < 2p$$

The valence electrons are layered upon a helium-like core, $[\text{He}] \equiv 1s^2$:

	Z	CONFIGURATION	BLOCK
Be	4	$[\text{He}]2s^2$	<i>s</i>
B	5	$[\text{He}]2s^22p^1$	<i>p</i>
C	6	$[\text{He}]2s^22p^2$	<i>p</i>
O	8	$[\text{He}]2s^22p^4$	<i>p</i>
Ne	10	$[\text{He}]2s^22p^6$	<i>p</i>

Elements in the *s* block have a valence configuration of either s^1 or s^2 . Elements in the *p* block have a valence configuration of s^2p^j , where $j = 1, 2, \dots, 6$.

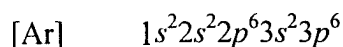
(b) These third-row atoms lie directly below the second-row atoms treated in (a). The same valence configurations recur, electron for electron, with the principal quantum number now increased from 2 to 3. The valence electrons fill the $3s$ and $3p$ orbitals surrounding a neonlike core, $[\text{Ne}] \equiv 1s^22s^22p^6$:

	Z	CONFIGURATION	BLOCK
Mg	12	$[\text{Ne}]3s^2$	<i>s</i>
Al	13	$[\text{Ne}]3s^23p^1$	<i>p</i>
Si	14	$[\text{Ne}]3s^23p^2$	<i>p</i>
S	16	$[\text{Ne}]3s^23p^4$	<i>p</i>
Ar	18	$[\text{Ne}]3s^23p^6$	<i>p</i>

(c) Here, in the fourth row, the selected atoms lie directly below those analyzed in (b). Ca ($Z = 20$) thus accepts two electrons in its $4s$ orbital, acquiring an $[\text{Ar}]4s^2$ configuration analogous to the $[\text{Ne}]3s^2$ configuration of Mg. Beyond calcium, however, the first series of transition metals intervenes, filling the $3d$ orbitals in the 10 elements from scandium through zinc. After Zn ($Z = 30$) comes Ga (with the configuration $[\text{Ar}]4s^23d^{10}4p^1$), following which the $4p$ orbitals are populated in the same way as shown previously:

	<i>Z</i>	CONFIGURATION	BLOCK
Ca	20	[Ar]4 <i>s</i> ²	<i>s</i>
Ga	31	[Ar]4 <i>s</i> ² 3 <i>d</i> ¹⁰ 4 <i>p</i> ¹	<i>P</i>
Ge	32	[Ar]4 <i>s</i> ² 3 <i>d</i> ¹⁰ 4 <i>p</i> ²	<i>P</i>
Se	34	[Ar]4 <i>s</i> ² 3 <i>d</i> ¹⁰ 4 <i>p</i> ⁴	<i>P</i>
Kr	36	[Ar]4 <i>s</i> ² 3 <i>d</i> ¹⁰ 4 <i>p</i> ⁶	<i>P</i>

The core configuration, isoelectronic with argon, contains 18 electrons:



22. The elements here are all transition metals, members of the *d* block.

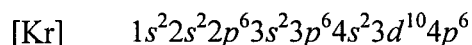
(a) These atoms are taken from the first transition series, in which up to 12 electrons are distributed among the 4*s* and 3*d* orbitals:

	<i>Z</i>	CONFIGURATION	BLOCK
SC	21	[Ar]4 <i>s</i> ² 3 <i>d</i> ¹	<i>d</i>
Ti	22	[Ar]4 <i>s</i> ² 3 <i>d</i> ²	<i>d</i>
V	23	[Ar]4 <i>s</i> ² 3 <i>d</i> ³	<i>d</i>
Fe	26	[Ar]4 <i>s</i> ² 3 <i>d</i> ⁶	<i>d</i>
Co	27	[Ar]4 <i>s</i> ² 3 <i>d</i> ⁷	<i>d</i>
Ni	28	[Ar]4 <i>s</i> ² 3 <i>d</i> ⁸	<i>d</i>

(b) This set of atoms, selected from the second transition series, lies directly underneath the set just considered-but, even so, the valence configurations do not match exactly. The **Aufbau** principle allows for certain anomalies in the buildup of these increasingly complex systems:

	<i>Z</i>	CONFIGURATION	BLOCK
Y	39	[Kr]5 <i>s</i> ² 4 <i>d</i> ¹	<i>d</i>
Zr	40	[Kr]5 <i>s</i> ² 4 <i>d</i> ²	<i>d</i>
Nb	41	[Kr]5 <i>s</i> ¹ 4 <i>d</i> ⁴	<i>d</i>
Ru	44	[Kr]5 <i>s</i> ¹ 4 <i>d</i> ⁷	<i>d</i>
Rh	45	[Kr]5 <i>s</i> ¹ 4 <i>d</i> ⁸	<i>d</i>
Pd	46	[Kr]4 <i>d</i> ¹⁰	<i>d</i>

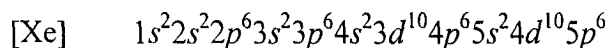
The atoms are all built on a 36-electron core isoelectronic with krypton:



(c) The specified atoms belong to the third transition series, with the 14 lanthanide elements interposed between lanthanum ($Z = 57$) and hafnium ($Z = 72$). Beginning with cerium ($Z = 58$), the seven $4f$ orbitals eventually accept 14 electrons before filling of the $4d$ orbitals resumes with hafnium. Note the anomalous configuration of platinum:

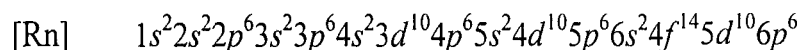
	Z	CONFIGURATION	BLOCK
La	57	[Xe] $6s^25d^1$	d
Hf	72	[Xe] $6s^24f^{14}5d^2$	d
Ta	73	[Xe] $6s^24f^{14}5d^3$	d
Os	76	[Xe] $6s^24f^{14}5d^6$	d
Ir	77	[Xe] $6s^24f^{14}5d^7$	d
Pt	78	[Xe] $6s^14f^{14}5d^9$	d

The xenonlike core,

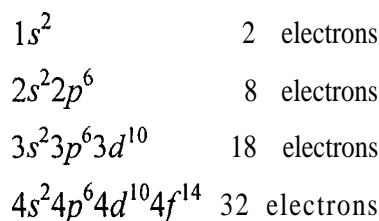


contains 54 electrons.

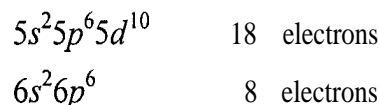
23. Seaborgium, element 106, contains 20 valence electrons beyond a radonlike core configuration (Rn, $Z = 86$):



The first four shells of the core are therefore fully occupied with 60 electrons,

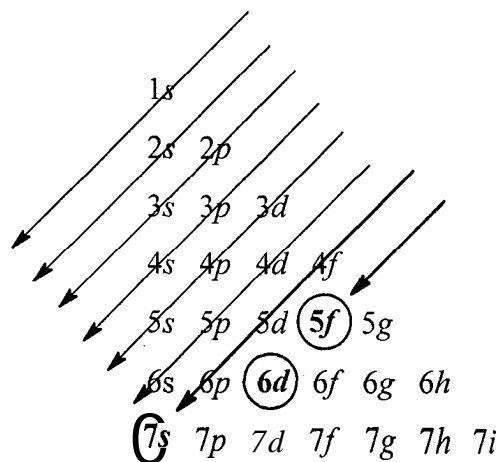


whereas the fifth and sixth shells are only partially filled:

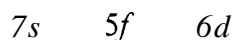


The $5f$ orbitals (capacity = 14 electrons), the $6d$ orbitals (capacity = 10 electrons), and the $6f$ orbitals (capacity = 14 electrons) are vacant, as are all orbitals in the seventh shell and higher.

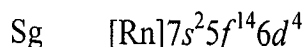
At this point, use the mnemonic device given in Figure 6-9 of *PoC* (page 201)



to predict that the next orbitals to be filled are



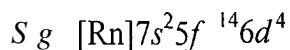
If so, then the 20 valence electrons in seaborgium should be distributed as follows:



The fifth-shell f orbitals are thus completely filled, while the sixth-shell d orbitals remain open. Seaborgium belongs to the d block.

Note that the $7s^26d^4$ configuration might possibly be rearranged to $7s^16d^5$. Lacking any further experimental information, however, we shall accept the $7s^26d^4$ state as a working model.

24. For convenience, locate seaborgium ($Z = 106$) in the seventh row of the periodic table and then proceed to add 12 electrons. Starting with the configuration determined in the preceding exercise,



the building-up sequence continues as

Bh	107	$[\text{Rn}]7s^25f^{14}6d^5$
Hs	108	$[\text{Rn}]7s^25f^{14}6d^6$
Mt	109	$[\text{Rn}]7s^25f^{14}6d^7$
Uun	110	$[\text{Rn}]7s^25f^{14}6d^8$
uuu	111	$[\text{Rn}]7s^25f^{14}6d^9$
Uub	112	$[\text{Rn}]7s^25f^{14}6d^{10}$

Element 112 ($6d^{10}$) thus completes the fourth transition series, and the next noble-gas atom should appear after six additional electrons enter to fill the $7p$ subshell. Counting through the p block in the seventh row, we come to element 118 (Uuo):

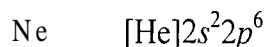


Note: Between the initial publication date of *PoC* and the preparation of this solutions manual, the discovery of elements 114, 116, and 118 has been announced.

Note also that elements with atomic number greater than 109 are temporarily designated by a three-letter symbol beginning with uppercase U.

25. Atoms in Groups VI and VII *gain* electrons to attain noble-gas configurations. Atoms in Groups I and II *lose* electrons.

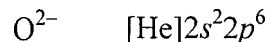
(a) All of the ions are isoelectronic with neon ($Z = 10$):



Take, for example, the $2s^22p^4$ ground-state configuration of neutral oxygen,

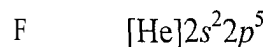


and add two electrons to create the doubly negative oxide anion:

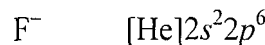


The extra electrons complete the p subshell.

Similarly, fluorine goes from



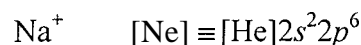
to



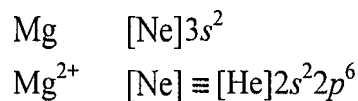
when one electron is added, whereas *removal* of one electron from



leaves the sodium cation:

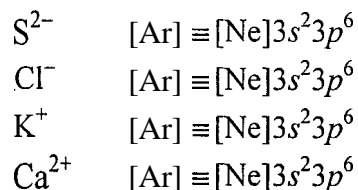


Removal of two electrons from magnesium, finally, produces the magnesium cation, again with a neonlike core:



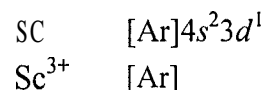
Notice how we can quickly deduce the configurations of both atoms and ions from their locations in the periodic table. With magnesium, say, we simply count backward by two positions to see that Mg^{2+} coincides with Ne. With oxygen, we advance by two positions to show that O^{2-} is also isoelectronic with Ne.

(b) These ions are the third-row and fourth-row counterparts of the species treated in (a). Each is isoelectronic with argon ($Z = 18$):

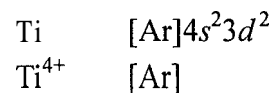


26. Each ion has been stripped down to its noble-gas core. Parts (a), (b), and (c) select the first three members, respectively, of the first, second, and third series of transition metals. See also Exercise 22.

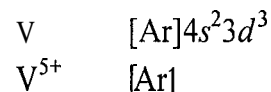
(a) Scandium, originally $4s^23d^1$, loses three electrons to become isoelectronic with argon as Sc^{3+} :



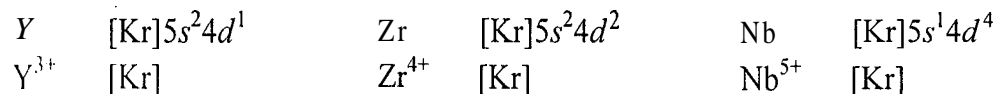
Titanium, with neutral configuration $[\text{Ar}]4s^23d^2$, likewise loses all four of its valence electrons to become Ti^{4+} :



The same argonlike result, too, is obtained for vanadium and its five valence electrons:



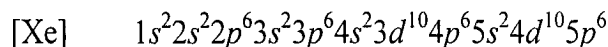
(b) These second-series transition metals ($4d$) lie directly beneath the $3d$ systems considered in (a). The parent atoms in each set have valence shells containing three, four, or five electrons, variously divided between s and p . Stripped clean, the ions are all isoelectronic with krypton ($Z = 36$):



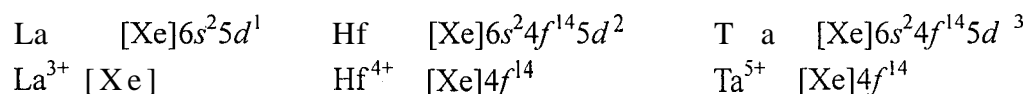
The neutral configuration of niobium differs slightly from that of vanadium, one row above, but the outcome after ionization is essentially the same. Five electrons, in all, are lost.

(c) A similar demonstration, this time for the first three members of the third transition series-but with a difference. Here the lanthanide elements intervene during the buildup, interposing 14 electrons between La (with a $5d^1$ configuration) and Hf (with a $5d^2$ configuration).

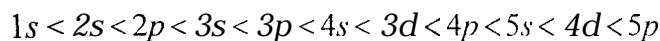
The La^{3+} ion is strictly isoelectronic with xenon ($Z = 54$),



whereas both Hf^{4+} and Ta^{5+} contain 14 additional electrons in their filled $4f$ subshells:

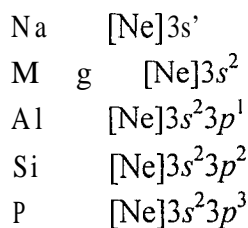


27. Bear in mind two considerations. First, the normal Aufbau sequence up through xenon is as follows:



Second, a neutral atom with atomic number Z contains Z electrons outside its nucleus.

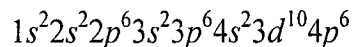
(a) Count five electrons beginning with Na in the third row, just after Ne. The $3s$ and $3p$ orbitals are filled in the usual way:



The element is phosphorus, atomic number 15.

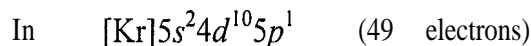
ALTERNATIVE SOLUTION: Note that the configuration specifies occupancies for a total of 15 electrons (core plus valence). If the structure is known to be neutral and monatomic, then its atomic number must also be 15.

(b) The 36-electron configuration



describes a krypton atom, built up in the normal order. Kr lies at the end of the fourth period, 18 electrons removed from Ar.

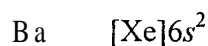
(c) Identify the atom as the first p-block element in the fifth row of the table—indium, atomic number 49:



Indium appears immediately after the $4d$ subshell is closed in cadmium ($Z = 48$), the last member of the second transition series.

28. Built on a xenonlike core, all three atoms fall in the sixth period.

(a) Barium, the second element beyond xenon, appears in the sixth row and second column of the table:

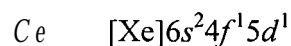


Its atomic number is 56.

(b) The configuration $[\text{Xe}]6s^25d^1$, with 57 electrons, denotes the element immediately following barium-lanthanum, the 57th element overall and the first transition metal in the third series:



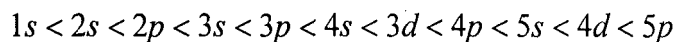
(c) Directly following lanthanum ($Z = 57$) is cerium ($Z = 58$), displayed in one of the 14-element extensions at the bottom of the table:



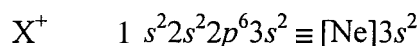
Beginning with this first *Zanthanide* element, the f block is opened. The first two valence electrons enter the s subshell, the third enters the d , and the fourth enters the f .

29. Similar to Exercise 27, but focused on ions rather than atoms: A cation X^{q+} has q electrons fewer than its parent atom X . An *anion* X^{q-} has q electrons more than X .

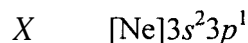
Orbitals are occupied in the usual sequence:



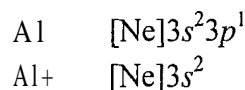
(a) Add one electron to the monovalent ion



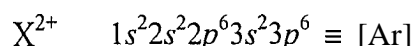
to regenerate the neutral atom X :



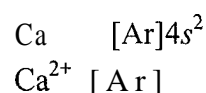
X therefore must be aluminum: atomic number 13, three elements past neon. The ion Al^+ , for its part, is isoelectronic with Mg, the neutral atom one position to the left of Al:



(b) Similar. Add two electrons to the doubly positive ion

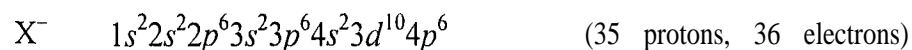


and thereby expose X as the element calcium ($Z = 20$):

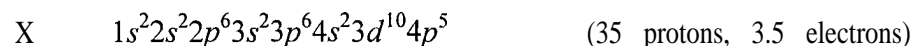


Calcium is situated two positions past argon.

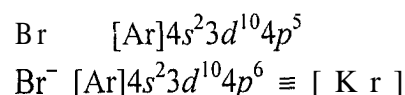
(c) The anion is isoelectronic with krypton. We remove one electron from the negative ion



to recover the neutral atom X, located one position to the left of krypton:

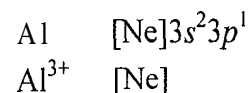


The atom is Br, and the ion is Br^- :



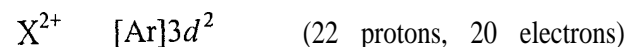
30. Use the same reasoning as in the preceding exercise.

(a) If a triply positive ion X^{3+} is isoelectronic with neon ($Z = 10$), then its parent atom X must contain 13 electrons:

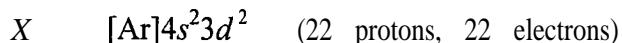


Aluminum ($Z = 13$) appears three positions beyond neon.

(b) The doubly positive ion

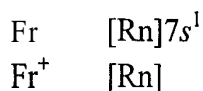


contains 20 electrons. The neutral parent atom contains 22:



We identify X as titanium, $Z = 22$.

(c) Count one position past radon, $Z = 86$, to obtain the neutral atom francium:



31. Look for ground-state orbitals to be filled in normal sequence,

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$

with the exclusion principle strictly observed: No more than two electrons—one with $m_s = \frac{1}{2}$ and one with $m_s = -\frac{1}{2}$ —may share the same spatial quantum numbers (n, ℓ, m_ℓ).

(a) The proposed configuration



places $3p$ erroneously before $2p$ and $3s$. The configuration predicted by the Aufbau principle, $1s^22s^22p^1$, describes the ground state of boron ($Z = 5$):



(b) The configuration



is inadmissible because the $1s$ and $2p$ orbitals remain vacant, despite the occupation of $3s$ and $3p$. The expected ground-state configuration for nine electrons is exemplified by fluorine ($Z = 9$):

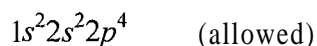


(c) With three electrons in the $2s$ orbital, the impossible configuration



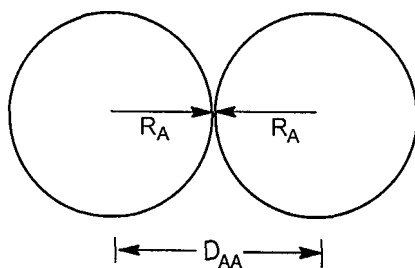
would violate the Pauli exclusion principle. Moreover, the $3p$ orbital would be improperly occupied before the $2p$ —another violation.

The expected configuration for eight electrons is displayed by oxygen ($Z=8$):



We begin a final group of exercises dealing with periodic trends in elemental properties. atomic radius, electron affinity, ionization energy. See Section 6-3 and Examples 6-5 through 6-8.

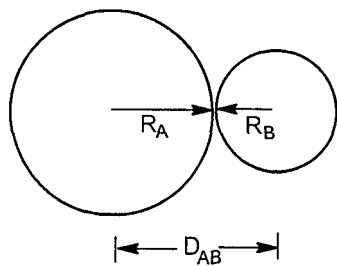
32. For a homonuclear diatomic molecule AA (see below),



we take the internuclear distance, D_{AA} , as twice the atomic radius:

$$D_{AA} = 2R_A$$

For a heteronuclear diatomic molecule AB,



we estimate D_{AB} as the sum of the two atomic radii:

$$D_{AB} \approx R_A + R_B$$

From the specified internuclear distances in H_2 and F_2 ,

$$D_{HH} = 0.7414 \text{ \AA}$$

$$D_{FF} = 1.4119 \text{ \AA}$$

we thus arrive at an approximate value of 1.08 \AA for D_{HF} , the bond length in HF:

$$R_{\text{H}} = \frac{1}{2}D_{\text{HH}} = 0.3707 \text{ \AA}$$

$$R_{\text{F}} = \frac{1}{2}D_{\text{FF}} = 0.7060 \text{ \AA}$$

$$D_{\text{HF}} \approx R_{\text{H}} + R_{\text{F}} = 1.0767 \text{ \AA} \quad (\sim 1.08 \text{ \AA})$$

The estimate, high by about 17%, is affected by the large difference in electronegativity between hydrogen and fluorine. The covalent interaction takes on a partial ionic character, leaving the bond stronger and shorter than otherwise expected.

For additional analysis of fractional ionic character, see Example 7-4 in *PoC* (page R7.8) and also Exercises 24 through 26 in Chapter 7. Atomic and ionic radii are discussed on pages 207-213 and considered further in Examples 6-5 and 6-6.

33. Use the same reasoning as in the preceding exercise:

$$D_{\text{HI}} \approx R_{\text{H}} + R_{\text{I}}$$

$$R_{\text{I}} \approx D_{\text{HI}} - R_{\text{H}} = 1.6090 \text{ \AA} - 0.3707 \text{ \AA} = 1.24 \text{ \AA}$$

34. For elements in the *s* and *pd* blocks, atomic radius usually decreases across a period and increases down a group. See pages 203-210 and also Example 6-5 (beginning on page R6.9 of *PoC*).

(a) Top to bottom, the three elements are all alkali metals (Group I):

$$R(\text{Li}) < R(\text{Rb}) < R(\text{Cs})$$

Lithium is in period 2. Rubidium is in period 5. Cesium is in period 6.

(b) Fluorine and lithium appear, respectively, near the far right and far left of the second period. Boron is in the middle:

$$R(\text{F}) < R(\text{B}) < R(\text{Li})$$

(c) Chlorine (in the third row) lies directly below fluorine (second row) in Group VII. Barium, found in period 6 of Group II, lies well toward the left and bottom of the table:

$$R(\text{F}) < R(\text{Cl}) < R(\text{Ba})$$

(d) Beryllium appears two periods above and one group to the right of potassium, whereas potassium sits directly above rubidium in Group I:

$$R(\text{Be}) < R(\text{K}) < R(\text{Rb})$$

(e) Chlorine (Group VII) lies four atoms to the right of aluminum (Group III) in the third period. Barium, in the sixth period, is found near the lower left-hand corner, in Group II:

$$R(\text{Cl}) < R(\text{Al}) < R(\text{Ba})$$

35. With fewer electrons than protons, a cation is more compact than its parent atom. Electron-nucleus attractions are enhanced, and electron-electron repulsions are diminished. The ion contracts.

An anion, gaining electrons, becomes larger than its parent atom. The increased repulsion between electrons forces the structure to expand.

See pages 2 11 and 2 13 of *PoC* and also Example 6-6 (page R6.10).

(a) We have a series that includes a neutral atom and two of its negative ions:

$$R(\text{O}) < R(\text{O}^-) < R(\text{O}^{2-})$$

The larger the negative charge, the larger the radius of the anion. The same number of protons-eight-must attract eight, nine, and ten electrons in going from 0 to O^- to O^{2-} .

(b) Li^+ , a cation, is smaller than its parent atom, Li. The beryllium atom, positioned immediately to the right of Li, is also smaller than the lithium atom, and the Be^{2+} ion is smaller than the contracted Li^+ ion as well:

$$R(\text{Be}^{2+}) < R(\text{Li}^+) < R(\text{Li})$$

Both Be^{2+} and Li^+ contain two electrons, but the beryllium nucleus has the greater positive charge and hence exerts the greater attractive potential.

(c) The cations follow the same trend as the neutral atoms-ionic radius decreases from left to right across a period. Each ion here is isoelectronic with neon, but the aluminum nucleus exercises the largest positive charge:

$$R(\text{Al}^{3+}) < R(\text{Mg}^{2+}) < R(\text{Na}^+)$$

(d) The radius of an anion, like the radius of its neutral parent atom, increases with principal quantum number down a group. Bromine, lying two rows below both fluorine and oxygen, produces the largest anion of the set: Br^- .

Although F^- and O^{2-} are both isoelectronic with neon, the fluorine nucleus has the greater positive charge. A fluoride ion is drawn in more tightly than an oxide ion:

$$R(\text{F}^-) < R(\text{O}^{2-}) < R(\text{Br}^-)$$

(e) The cations follow the same trend as the parent atoms. Radius increases down a group and decreases across a period:

$$R(\text{Al}^{3+}) < R(\text{Ba}^{2+}) < R(\text{Cs}^+)$$

Aluminum is in the third period. Barium is in the sixth period, immediately to the right of cesium.

36. Trends in electron affinity are similar to trends in radius and ionization energy, albeit not quite as regular. See pages 213-215 in *PoC* and also Example 6-8 (page R6.11).

(a) Fluorine shows the strongest affinity for an extra electron, the addition of which takes it from a seven-electron $2s^2 2p^5$ configuration to a neonlike $2s^2 2p^6$ state: a Lewis octet.

Lithium, able to fill its 2s orbital by adding an electron, has a modest electron affinity. Li^- is sufficiently stable to exist as $2s^2$, but the extra electron is bound far more weakly than the one in F^- .

To add yet another electron to Li^- —and thus open up the 2p subshell—would cost energy, not release it. The Li^- anion does not have a favorable electron affinity:

$$EA(\text{Li}^-) < EA(\text{Li}) < EA(\text{F})$$

(b) Again, fluorine is best able to accept an extra electron and thereby obtain a noble-gas configuration. Nitrogen, by contrast, has no such affinity, presumably because its half-filled $2s^2 2p^3$ configuration is energetically favored over $2s^2 2p^4$.

Oxygen, falling between these two extremes, does have a fairly strong affinity for one more electron. Its higher effective nuclear charge relative to nitrogen helps stabilize the O^- anion. The overall trend is as follows:

$$EA(\text{N}) < EA(\text{O}) < EA(\text{F})$$

(c) Calcium, more stable with its existing s^2 configuration (a filled s orbital) than with an $s^2 p^1$ configuration (an open shell), shows no electron affinity. Chlorine has the strongest electron affinity, owing to the same reasons given for fluorine in (a) above. Sulfur, like oxygen in the second row, has a moderately strong affinity. Its relatively high effective nuclear charge helps stabilize the S^- anion:

$$EA(\text{Ca}) < EA(\text{S}) < EA(\text{Cl})$$

(d) Compare the positions of Ba and Ca in the periodic table, as well as those of I and Cl. The resulting trend in electron affinity parallels the one noted in (c) above: Ba (Group II) has zero affinity, whereas I (Group VII) has a strong affinity.

Thallium, with a singlep electron but a large atomic radius, has a slight affinity for one more:

$$EA(\text{Ba}) < EA(\text{Tl}) < EA(\text{I})$$

(e) The atoms are all halogens-members of Group VII, with ns^2np^5 valence configurations. Astatine is in period 6. Iodine is in period 5. Bromine is in period 4.

Although there are exceptions, electron affinity usually increases going up a group. The atoms grow smaller, and consequently more energy is released upon attachment of an electron:

$$EA(\text{At}) < EA(\text{I}) < EA(\text{Br})$$

37. The smaller the atom, the more tightly bound is the valence electron. Ionization energies typically increase from left to right across a period and decrease from top to bottom down a group.

In addition, it costs more energy to pull a second electron from an already ionized atom (X'), and it costs still more to remove a third electron from a doubly ionized atom (X^{2+}). Second ionization energies (I_2) are higher than first ionization energies (I_1). Third ionization energies are higher than second ionization energies. Fourth ionization energies are higher than third ionization energies. And so on.

See *PoC*, pages 210-212 and Example 6-7 (page R6.10).

(a) Beryllium, smaller than lithium, has the larger first ionization energy. Nevertheless, a second ionization of lithium, from Li^+ to Li^{2+} , is costlier by far. To ionize Li^+ entails the disruption of a helium-like $1s^2$ configuration as well as the removal of a tightly bound electron from the shrunken Li^+ cation.

I_2 for lithium is the largest ionization energy of the set.

(b) The *first* ionization energy of sodium already exceeds the first ionization energy of rubidium. The *seventh* ionization of sodium, from Na^{6+} to Na^{7+} , should require an enormous amount of energy-presumably much greater than the amount needed for a second ionization of cesium.

I_7 for sodium is larger than either I_2 for cesium or I_1 for rubidium.

(c) I_3 for zirconium, a third ionization, is larger than the two first ionization energies cited.

38. The Pauli exclusion principle prevents two electrons from occupying the same quantum state-forcing them, instead, to spread out over different regions in space. The effect is manifest in the hierarchical structures of all atoms and molecules, wherein different electrons have different average energies and positions. Electrons are pushed progressively farther away from the nucleus and thus become easier to detach.

Without the energetic layering imposed by exclusion, there would be no loosely bound, highly reactive valence region where electrons might easily bring about chemical recombination. In a nonexclusionary world, all the electrons would be trapped near the nucleus in the same state.