**Nuclear reactions?** (a)  ${}_{7}^{14}$  N +  ${}_{2}^{4}$  He? You can tackle these questions easily if you do an accounting of protons and neutrons right away. The nuclear reactants  ${}^{14}$ N and  ${}^{4}$ He together contain 9 protons (7 + 2) and 9 neutrons. You are told that one of the products is  ${}^{17}$ O, which contains 8 protons and 9 neutrons. (Remember, you can tell how many protons an atom contains by consulting a periodic table and noting its atomic number.) Therefore, since one proton is not yet accounted for on the right hand side of the equation, the balanced equation is:

$${}^{14}_7 \text{ N} + {}^4_2 \text{ He} \rightarrow {}^{17}_8 \text{ } \mathcal{O} + {}^1_1 \text{ p} + \gamma$$

(b)  ${}_{6}^{12}$  C + p? The atomic number of carbon is 6. If you add one proton to a carbon nucleus, the product must be the nucleus of the element with an atomic number of 6 + 1 = 7, which of course is a nitrogen nucleus. Remember, the mass number will also increase whenever a proton, or a neutron, is added to a nucleus and no subsequent fission occurs. Therefore, the product is a  ${}^{13}$ N nucleus and the balanced equation is:

$$\frac{12}{6}C + \frac{1}{1}p \rightarrow \frac{13}{7}N + \gamma$$

(c)  $\frac{14}{7}$  N +  $\frac{1}{6}$  n? Here you are told that the products are  $\frac{3}{1}$  H and  $\frac{12}{6}$  C. You should confirm that the equation

$${}^{14}_7 \text{ N} + {}^1_0 \text{ n} \rightarrow {}^{12}_6 \text{ C} + {}^3_1 \text{ H}$$

is indeed balanced. The reactants together contain 7 protons and 8 neutrons (7 + 1). The products also contain 7 protons (1 + 6) and 8 neutrons (2 + 6). Therefore, the equation is balanced.

1.2  $_{10}^{22}$  Ne + a? Use the accounting procedure described in the answer to Exercise 1.1 above. Neon has atomic number 10 (therefore 10 protons) and magnesium has atomic number 12 (12 protons). In Section 1.1, *Nucleosynthesis of light elements*, you learned that an  $\alpha$  particle is a helium-4 nucleus, <sup>4</sup>He. Therefore, the nuclear reactants together contain 12 protons (10 + 2) and 14 neutrons (12 + 2). One of the products is a  $_{12}^{25}$  Mg nucleus, which contains 12 protons and 13 neutrons. Since one neutron is not yet accounted for, it must appear as a product, and the balanced nuclear equation is:

$${}^{22}_{10} \operatorname{Ne} + {}^{4}_{2} \operatorname{He} \to {}^{25}_{12} \operatorname{Mg} + {}^{1}_{0} \operatorname{n}$$

- **1.3 Draw the periodic table?** See Figure 1.4 and the inside front cover of this book. You should start learning the names and positions of elements that you do not know. Start with the alkali metals and the alkaline earths. Then learn the elements in the p block. A blank periodic table can be found on the inside back cover of this book. You should make several photocopies of it and should test yourself from time to time, especially after studying each chapter.
- **E(He<sup>+</sup>)/E(Be<sup>3+</sup>)?** The ground-state energy of a hydrogenic ion, like He<sup>+</sup> or Be<sup>3+</sup>, is defined as the orbital energy of its single electron, which is given by Equations 1.4 and 1.5:

$$E = Z^2 m_e e^4 / 32 \pi^2 (\varepsilon_0)^2 (h/2\pi)^2 n^2$$

For the ratio  $E(\text{He}^+)/E(\text{Be}^{3+})$ , the constants can be ignored, and:

$$E(\text{He}^+)/E(\text{Be}^{3+}) = Z(\text{He}^+)^2/Z(\text{Be}^{3+})^2 = 2^2/4^2 = 0.25$$

E(H, n = 1) - E(H, n = 6)? The expression for E given in Equations 1.4 and 1.5 (see above) can be used for a hydrogen atom as well as for hydrogenic ions. The ratio E(H, n = 1)/E(H, n = 6) can be determined as follows:

$$E(H, n = 1)/E(H, n = 6) = (1/1^2)/(1/6^2) = 36$$

Therefore, E(H, n = 6) = (E(H, n = 1))/36 = -0.378 eV, and the difference is:

$$E(H, n = 1) - E(H, n = 6) = -13.2 \text{ eV}$$

1.1



Whereas the radial distribution function for a 1s orbital has a single maximum, that for a 2s orbital has two maxima and a minimum (at  $r = 2a_0/Z$  for hydrogenic 2s orbitals). The presence of the node at  $r = 2a_0/Z$  for  $\psi(2s)$  requires the presence of the two maxima and the minimum in the 2s radial distribution function. Using the same reasoning, the absence of a radial node for  $\psi(2p)$  requires that the 2p radial distribution function have only a single maximum, as shown in Figure 1.14 and below:



The angular wavefunctions are the familiar pictures that chemists draw to represent s, p, d, and f orbitals, such as the ones in Figures 1.15-1.18. The familiar nodal plane for a 2p orbital is a property the orbital possesses because of the mathematical form of its angular wavefunction, not because of the mathematical form of its radial wavefunction.

1.11

I(Ca) vs. I(Zn)? The first ionization energies of calcium and zinc are 6.11 and 9.39 eV, respectively (see Appendix 1). Both of these atoms have an electron configuration that ends with  $4s^2$ : Ca is  $[Ar]4s^2$  and Zn is  $[Ar]3d^{10}4s^2$ . An atom of zinc has 30 protons in its nucleus and an atom of calcium has 20, so clearly zinc has a higher nuclear charge than calcium. Remember, though, that it is *effective* nuclear charge ( $Z_{eff}$ ) that directly affects the ionization energy of an atom. Since I(Zn) > I(Ca), it would seem that  $Z_{eff}(Zn) > Z_{eff}(Ca)$ . How can you demonstrate that this is as it should be? The actual nuclear charge can always be readily determined by looking at the periodic table and noting the atomic number of an atom. The effective nuclear charge cannot be directly determined, i.e., it requires some interpretation on your part. Read Section 1.6, *Penetration and shielding*, again. Study the trend for the period 2 *p*-block elements in Table 1.3. The pattern that emerges is that not only Z but also  $Z_{eff}$  rises from boron to neon. Each successive element has one additional proton in its nucleus and one additional electron to balance the charge. However, the additional electron never completely shields the other electrons in the atom. Therefore,  $Z_{eff}$  rises from B to Ne. Similarly,  $Z_{eff}$  rises through the *d* block from Se to Zn, and that is why  $Z_{eff}(Ca) > Z_{eff}(Ca)$ .

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- **1.12** I(Sr) vs. I(Ba) vs. I(Ra)? The first ionization energies of strontium, barium, and radium are 5.69, 5.21, and 5.28 eV, respectively (see Table 1.6). Normally, atomic radius increases and ionization energy decreases down a group in the periodic table. However, in this case I(Ba) < I(Ra). Study the periodic table, especially the alkaline earths. Notice that Ba is eighteen elements past Sr, but Ra is thirty-two elements past Ba. The difference between the two corresponds to the fourteen 4*f* elements between Ba and Lu. As explained above in the answer to Exercise 1.9,  $Z_{eff}$  rises with each successive element because of incomplete shielding. Therefore, even though radium would be expected to have a larger radius than barium, it has a higher first ionization energy because it has such a large  $Z_{eff}$ .
- 1.13  $I_2$  of some period 4 elements? The second ionization energies of the elements calcium through manganese increase from left to right in the periodic table with the exception that  $I_2(Cr) > I_2(Mn)$ . The electron configurations of the elements are:

CaScTiVCrMn $[Ar]4s^2$  $[Ar]3d^14s^2$  $[Ar]3d^24s^2$  $[Ar]3d^34s^2$  $[Ar]3d^54s^1$  $[Ar]3d^54s^2$ 

Both the first and the second ionization processes remove electrons from the 4s orbital of these atoms, with the exception of Cr. In general, the 4s electrons are poorly shielded by the 3d electrons, so  $Z_{eff}(4s)$  increases from left to right and  $I_2$  also increases from left to right. While the  $I_1$  process removes the sole 4s electron for Cr, the  $I_2$  process must remove a 3d electron. The higher value of  $I_2$  for Cr relative to Mn is a consequence of the special stability of half-filled subshell configurations.

**1.14** Ground-state electron configurations? (a) C? Four elements past He. Helium ends period 1; therefore carbon is  $[He]2s^22p^2$ .

(b) F? Seven elements past He; therefore  $[He]2s^22p^5$ .

(c) Ca? Two elements past Ar, which ends period 3, leaving the 3d subshell empty; therefore  $[Ar]4s^2$ .

(d)  $Ga^{3+}$ ? Thirteen elements, but only ten electrons, past Ar, and since it is a cation, there is no doubt that E(3d) < E(4s); therefore [Ar] $3d^{10}$ .

(e) Bi? Twenty-nine elements past Xe, which ends period 5, leaving the 5d and the 4f subshells empty; therefore  $[Xe]4f^{4}5d^{10}6s^{2}6p^{3}$ .

(f)  $Pb^{2+}$ ? Twenty-eight elements, but only twenty-six electrons, past Xe, which ends period 5, leaving the 5d and the 4f subshells empty; therefore  $[Xe]4f^{4}5d^{10}6s^{2}$ .

1.15 More ground-state electron configurations? (a) Sc? Three elements past Ar; therefore  $[Ar]3d^{1}4s^{2}$ .

(b)  $V^{3+}$ ? Five elements, but only two electrons, past Ar, and since it is a cation, there is no doubt that E(3d) < E(4s); therefore [Ar] $3d^2$ .

(c)  $Mn^{2+2}$  Seven elements, but only five electrons, past Ar; therefore [Ar] $3d^5$ .

(d)  $Cr^{2+}$ ? Six elements, but only four electrons, past Ar; therefore [Ar] $3d^4$ .

(e)  $Co^{3+}$ ? Nine elements, but only six electrons, past Ar; therefore [Ar] $3d^6$ .

(f)  $Cr^{6+}$ ? Six elements past Ar, but with a +6 charge it has the *same* electron configuration as Ar, which is written as [Ar]. Sometimes inorganic chemists will write the electron configuration as [Ar] $3a^0$  to emphasize that there are no *d* electrons for this *d*-block metal ion in its highest oxidation state.

The relative sizes of  $Cr^{6+}$ ,  $[Ar]3d^{0}$ , and  $Cr^{2+}$ ,  $[Ar]3d^{4}$ :



(g) Cu? Eleven elements past Ar, but its electron configuration is not  $[Ar]3d^94s^2$ . The special stability experienced by completely filled subshells causes the actual electron configuration of Cu to be  $[Ar]3d^{10}4s^1$ .

(h)  $Gd^{3+}$ ? Ten elements, but only seven electrons, past Xe, which ends period 5 leaving the 5d and the 4f subshells empty; therefore  $[Xe]4f^7$ .

1.16

More ground-state electron configurations? (a) W? Twenty elements past Xe, fourteen of which are the 4f elements. If you assumed that the configuration would resemble that of chromium, you would write  $[Xe]4/^{45}d^{5}6s^{1}$ . It turns out that the actual configuration is  $[Xe]4/^{45}d^{4}6s^{2}$ . The configurations of the heavier dand f-block elements show some exceptions to the trends for the lighter d-block elements.

(b)  $Rh^{3+2}$  Nine elements, but only six electrons, past Kr; therefore [Kr]4 $d^6$ .

(c)  $Eu^{3+}$ ? Nine elements, but only six electrons, past Xe, which ends period 5, leaving the 5d and the 4f subshells empty; therefore [Xe]4f.

(d) Eu<sup>2+</sup>? This will have one more electron than Eu<sup>3+</sup>. Therefore, the ground-state electron configuration of  $Eu^{2+}$  is [Xe]4f.

(e) V<sup>5+</sup>? Five elements past Ar, but with a 5+ charge it has the same electron configuration as Ar, which is written as [Ar] or  $[Ar]3d^{0}$ .

(f) Mo<sup>4+</sup>? Six elements, but only two electrons, past Kr; therefore [Kr] $4d^2$ .

1.17 Identify the elements?

- (a) S
- (b) Sr
- (c) V
- (d) Tc
- (e) In
- (f) Sm

 $I_1, A_e$ , and  $\chi$  for period 3? The following values were taken from Tables 1.6, 1.7, and 1.8: 1.18

Element	Electron configuration	$I_1(eV)$	$A_{\rm e}({\rm eV})$	χ	
Na	[Ne]3s	5.14	0.548	0.93	
Mg	$[Ne]3s^2$	7.64	-0.4	1.31	
AI	$[Ne]3s^23p^1$	5.98	0.441	1.61	
Si	$[Ne]3s^23p^2$	8.15	1.385	1.90	
Р	$[Ne]3s^23p^3$	11.0	0.747	2.19	
S	$[Ne]3s^23p^4$	10.36	2.077	2.58	
Cl	$[Ne]3s^23p^5$	13.10	3.617	3.16	2
Ar	$[Ne]3s^23p^6$	15.76	-1.0		

In general,  $I_1$ ,  $A_e$ , and  $\chi$  all increase from left to right across period 3 (or from top to bottom in the table above). All three quantities reflect how tightly an atom holds on to its electrons, or how tightly it holds on to additional electrons. The cause of the general increase across the period is the gradual increase in  $Z_{eff}$ , which itself is caused by the incomplete shielding of electrons of a given value of n by electrons with the same n. The exceptions are explained as follows:  $I_1$  (Mg) >  $I_1$ (Al) and  $A_e$ (Na) > $A_e$ (Al)—both of these are due to the greater stability of 3s electrons relative to 3p electrons;  $A_e(Mg)$  and  $A_e(Ar) < 0$ —filled subshells impart a special stability to an atom or ion (in these two cases the additional electron must be added to a higher energy subshell (for Mg) or shell (for Ar));  $I_1(P) > I_1(S)$  and  $A_e(Si) > A_e(P)$ —the loss of an electron from S and the gain of an additional electron by Si both result in an ion with a half-filled p subshell, which, like filled subshells, imparts a special stability to an atom or ion.

1.19 Metallic radii of Nb and Ta? If you look at the elements just before these two in Table 1.4, you will see that this is a general trend. Normally, the period 6 elements would be expected to have larger metallic radii than their period 5 vertical neighbors; only Cs and Ba follow this trend: Cs is larger than Rb and Ba is larger than Sr. Lutetium, Lu, is significantly smaller than yttrium, Y, and Hf is just barely the same size as Zr. After Nb and Ta, the "normal" expectation is observed. There are no intervening elements between Sr and Y, but there are fourteen intervening elements, the lanthanides, between Ba and Lu. A contraction of the radii of the

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1.20

elements starting with Lu is due to incomplete shielding by the 4f electrons. For a more detailed discussion of this concept, study Section 1.9(a), Atomic and ionic radii.

Electronegativities across period 2? Plots of electronegativity across period 2 and ionization energies across period 2 are superimposed on the figure below. The general trend is the same in both plots; both  $\chi$  and  $I_1$  increase from left to right across a period, and this is because the effective nuclear charge increases for the n = 2 orbitals across period 2. The two deviations in the upper plot result from different phenomena. For boron, the outermost electron occupies a 2p orbital, which has a higher energy than a beryllium atom's 2s orbital. The higher energy of the 2p electron offsets a boron atom's greater nuclear charge. For oxygen, two electrons are paired in one of the 2p orbitals, and the mutual repulsion they experience offsets an oxygen atom's greater nuclear charge relative to a nitrogen atom. Even though this exercise did not require the use of electron affinity values (Table 1.7), it is useful to think about the "connections" between the various atomic properties. Note that the electron affinities of beryllium and nitrogen are negative, and the explanation for these apparent anomalies is the same as the explanation given above for the departure of  $I_1(B)$  and  $I_1(O)$  from the general upward trend.



- 1.21 Frontier orbitals of Be? Recall from Section 1.9(c), *Electron affinity*, that the frontier orbitals are the highest occupied and the lowest unoccupied orbitals of a chemical species (atom, molecule, or ion). Since the ground-state electron configuration of a beryllium atom is  $1s^22s^2$ , the frontier orbitals are the 2s orbital (highest occupied) and the 2p orbitals (lowest unoccupied). Note that there can be more than two frontier orbitals if either the highest occupied and/or lowest unoccupied energy levels are degenerate.
- 1.22 Broad trends in *I*, atomic radius, and electronegativity? In general, as you move across a period from left to right, the ionization energy *I* increases, the atomic radius decreases, and the electronegativity increases. All three trends are the result of the increase in effective nuclear charge  $Z_{\text{eff}}$  from left to right.

- 1:10 2s electrons are being shielded by 1s electrons They are being sheilded from the nucleus (specifically the + charge from the protons).
- 1111 See answer in 1113. Mn<sup>2r</sup>is [Ar] 3d<sup>5</sup>, which is half filled, thus it gains stability upon lose Cr<sup>2t</sup> does not gain this extra stability

1:12.

dxy dx2-yz