

CHAPTER 1

CHEMICAL FOUNDATIONS

Questions

11. A law summarizes what happens, e.g., law of conservation of mass in a chemical reaction or the ideal gas law, $PV = nRT$. A theory (model) is an attempt to explain why something happens. Dalton's atomic theory explains why mass is conserved in a chemical reaction. The kinetic molecular theory explains why pressure and volume are inversely related at constant temperature and moles of gas present, as well as explaining the other mathematical relationships summarized in $PV = nRT$.
12. a. At 8 a.m., approximately 57 cars pass through the intersection per hour.
b. At 12 a.m. (midnight), only 1 or 2 cars pass through the intersection per hour.
c. Traffic at the intersection is limited to less than 10 cars per hour from 8 p.m. to 5 a.m. Starting at 6 a.m., there is a steady increase in traffic through the intersection, peaking at 8 a.m. when approximately 57 cars pass per hour. Past 8 a.m. traffic moderates to about 40 cars through the intersection per hour until noon, and then decreases to 21 cars per hour by 3 p.m. Past 3 p.m. traffic steadily increases to a peak of 52 cars per hour at 5 p.m., and then steadily decreases to the overnight level of less than 10 cars through the intersection per hour.
d. The traffic pattern through the intersection is directly related to the work schedules of the general population as well as to the store hours of the businesses in downtown.
e. Run the same experiment on a Sunday, when most of the general population doesn't work and when a significant number of downtown stores are closed in the morning.
13. The fundamental steps are
(1) making observations;
(2) formulating hypotheses;
(3) performing experiments to test the hypotheses.

The key to the scientific method is performing experiments to test hypotheses. If after the test of time the hypotheses seem to account satisfactorily for some aspect of natural behavior, then the set of tested hypotheses turns into a theory (model). However, scientists continue to perform experiments to refine or replace existing theories. Hence, science is a dynamic or active process, not a static one.

14. A compound will always contain the same numbers (and types) of atoms. A given amount of hydrogen will react only with a specific amount of oxygen. Any excess oxygen will remain unreacted.
15. Law of conservation of mass: Mass is neither created nor destroyed. The total mass before a chemical reaction always equals the total mass after a chemical reaction.

Law of definite proportion: A given compound always contains exactly the same proportion of elements by mass. For example, water is always 1 g H for every 8 g oxygen.

Law of multiple proportions: When two elements form a series of compounds, the ratios of the mass of the second element that combine with 1 g of the first element always can be reduced to small whole numbers. For CO_2 and CO discussed in Section 1.4, the mass ratios of oxygen that react with 1 g carbon in each compound are in a 2 : 1 ratio.

16. Yes, 1.0 g H would react with 37.0 g ^{37}Cl , and 1.0 g H would react with 35.0 g ^{35}Cl .

No, the mass ratio of H/Cl would always be 1 g H/37 g Cl for ^{37}Cl and 1 g H/35 g Cl for ^{35}Cl . As long as we had pure ^{37}Cl or pure ^{35}Cl , the ratios will always hold. If we have a mixture (such as the natural abundance of chlorine), the ratio will also be constant as long as the composition of the mixture of the two isotopes does not change.

17. Natural niacin and commercially produced niacin have the exact same formula of $\text{C}_6\text{H}_5\text{NO}_2$. Therefore, both sources produce niacin having an identical nutritional value. There may be other compounds present in natural niacin that would increase the nutritional value, but the nutritional value due to just niacin is identical to the commercially produced niacin.

18. a. The smaller parts are electrons and the nucleus. The nucleus is broken down into protons and neutrons, which can be broken down into quarks. For our purpose, electrons, neutrons, and protons are the key smaller parts of an atom.
- b. All atoms of hydrogen have 1 proton in the nucleus. Different isotopes of hydrogen have 0, 1, or 2 neutrons in the nucleus. Because we are talking about atoms, this implies a neutral charge, which dictates 1 electron present for all hydrogen atoms. If charged ions were included, then different ions/atoms of H could have different numbers of electrons.
- c. Hydrogen atoms always have 1 proton in the nucleus, and helium atoms always have 2 protons in the nucleus. The number of neutrons can be the same for a hydrogen atom and a helium atom. Tritium (^3H) and ^4He both have 2 neutrons. Assuming neutral atoms, then the number of electrons will be 1 for hydrogen and 2 for helium.
- d. Water (H_2O) is always 1 g hydrogen for every 8 g of O present, whereas H_2O_2 is always 1 g hydrogen for every 16 g of O present. These are distinctly different compounds, each with its own unique relative number and types of atoms present.
- e. A chemical equation involves a reorganization of the atoms. Bonds are broken between atoms in the reactants, and new bonds are formed in the products. The number and types of atoms between reactants and products do not change. Because atoms are conserved in a chemical reaction, mass is also conserved.

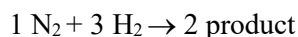
19. J. J. Thomson's study of cathode-ray tubes led him to postulate the existence of negatively charged particles that we now call electrons. Ernest Rutherford and his alpha bombardment of metal foil experiments led him to postulate the nuclear atom—an atom with a tiny dense center of positive charge (the nucleus) with electrons moving about the nucleus at relatively large distances away; the distance is so large that an atom is mostly empty space.

20. The atom is composed of a tiny dense nucleus containing most of the mass of the atom. The nucleus itself is composed of neutrons and protons. Neutrons have a mass slightly larger than that of a proton and have no charge. Protons, on the other hand, have a 1+ relative charge as compared to the 1- charged electrons; the electrons move about the nucleus at relatively large distances. The volume of space that the electrons move about is so large, as compared to the nucleus, that we say an atom is mostly empty space.
21. The number and arrangement of electrons in an atom determine how the atom will react with other atoms. The electrons determine the chemical properties of an atom. The number of neutrons present determines the isotope identity.
22. Density = mass/volume; if the volumes are assumed equal, then the much more massive proton would have a much larger density than the relatively light electron.
23. For lighter, stable isotopes, the number of protons in the nucleus is about equal to the number of neutrons. When the number of protons and neutrons is equal to each other, the mass number (protons + neutrons) will be twice the atomic number (protons). Therefore, for lighter isotopes, the ratio of the mass number to the atomic number is close to 2. For example, consider ^{28}Si , which has 14 protons and $(28 - 14 =)$ 14 neutrons. Here, the mass number to atomic number ratio is $28/14 = 2.0$. For heavier isotopes, there are more neutrons than protons in the nucleus. Therefore, the ratio of the mass number to the atomic number increases steadily upward from 2 as the isotopes get heavier and heavier. For example, ^{238}U has 92 protons and $(238 - 92 =)$ 146 neutrons. The ratio of the mass number to the atomic number for ^{238}U is $238/92 = 2.6$.
24. Some elements exist as molecular substances. That is, hydrogen normally exists as H_2 molecules, not single hydrogen atoms. The same is true for N_2 , O_2 , F_2 , Cl_2 , Br_2 , and I_2 .

Exercises

Development of the Atomic Theory

25. a. The composition of a substance depends on the numbers of atoms of each element making up the compound (depends on the formula of the compound) and not on the composition of the mixture from which it was formed.
- b. Avogadro's hypothesis (law) implies that volume ratios are equal to molecule ratios at constant temperature and pressure. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$. From the balanced equation, the volume of HCl produced will be twice the volume of H_2 (or Cl_2) reacted.
26. Avogadro's hypothesis (law) implies that volume ratios are equal to molecule ratios at constant temperature and pressure. Here, 1 volume of N_2 reacts with 3 volumes of H_2 to produce 2 volumes of the gaseous product or in terms of molecule ratios:



In order for the equation to be balanced, the product must be NH_3 .

27. From the law of definite proportions, a given compound always contains exactly the same proportion of elements by mass. The first sample of chloroform has a total mass of 12.0 g C + 106.4 g Cl + 1.01 g H = 119.41 g (carrying extra significant figures). The mass percent of carbon in this sample of chloroform is:

$$\frac{12.0 \text{ g C}}{119.41 \text{ g total}} \times 100 = 10.05\% \text{ C by mass}$$

From the law of definite proportions, the second sample of chloroform must also contain 10.05% C by mass. Let x = mass of chloroform in the second sample:

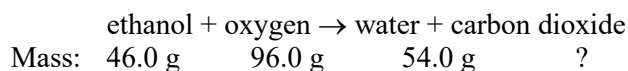
$$\frac{30.0 \text{ g C}}{x} \times 100 = 10.05, x = 299 \text{ g chloroform}$$

28. A compound will always have a constant composition by mass. From the initial data given, the mass ratio of H : S : O in sulfuric acid (H_2SO_4) is:

$$\frac{2.02}{2.02} : \frac{32.07}{2.02} : \frac{64.00}{2.02} = 1 : 15.9 : 31.7$$

If we have 7.27 g H, then we will have $7.27 \times 15.9 = 116 \text{ g S}$ and $7.27 \times 31.7 = 230. \text{ g O}$ in the second sample of H_2SO_4 .

29. Mass is conserved in a chemical reaction because atoms are conserved. Chemical reactions involve the reorganization of atoms, so formulas change in a chemical reaction, but the number and types of atoms do not change. Because the atoms do not change in a chemical reaction, mass must not change. In this equation we have two oxygen atoms and four hydrogen atoms both before and after the reaction occurs.
30. Mass is conserved in a chemical reaction.



Mass of reactants = 46.0 + 96.0 = 142.0 g = mass of products

$$142.0 \text{ g} = 54.0 \text{ g} + \text{mass of CO}_2, \text{ mass of CO}_2 = 142.0 - 54.0 = 88.0 \text{ g}$$

31. To get the atomic mass of H to be 1.00, we divide the mass of hydrogen that reacts with 1.00 g of oxygen by 0.126; that is, $\frac{0.126}{0.126} = 1.00$. To get Na, Mg, and O on the same scale, we do the same division.

$$\text{Na: } \frac{2.875}{0.126} = 22.8; \text{ Mg: } \frac{1.500}{0.126} = 11.9; \text{ O: } \frac{1.00}{0.126} = 7.94$$

	H	O	Na	Mg
Relative value	1.00	7.94	22.8	11.9
Accepted value	1.008	16.00	22.99	24.31

For your information, the atomic masses of O and Mg are incorrect. The atomic masses of H and Na are close to the values given in the periodic table. Something must be wrong about the assumed formulas of the compounds. It turns out the correct formulas are H_2O , Na_2O , and MgO . The smaller discrepancies result from the error in the assumed atomic mass of H.

32. If the formula is InO, then one atomic mass of In would combine with one atomic mass of O, or:

$$\frac{A}{16.00} = \frac{4.784 \text{ g In}}{1.000 \text{ g O}}, A = \text{atomic mass of In} = 76.54$$

If the formula is In₂O₃, then two times the atomic mass of In will combine with three times the atomic mass of O, or:

$$\frac{2A}{(3)16.00} = \frac{4.784 \text{ g In}}{1.000 \text{ g O}}, A = \text{atomic mass of In} = 114.8$$

The latter number is the atomic mass of In used in the modern periodic table.

The Nature of the Atom

33. From section 1-7, the nucleus has “a diameter of about 10^{-13} cm” and the electrons “move about the nucleus at an average distance of about 10^{-8} cm from it.” We will use these statements to help determine the densities. Density of hydrogen nucleus (contains one proton only):

$$V_{\text{nucleus}} = \frac{4}{3} \pi r^3 = \frac{4}{3} (3.14) (5 \times 10^{-14} \text{ cm})^3 = 5 \times 10^{-40} \text{ cm}^3$$

$$d = \text{density} = \frac{1.67 \times 10^{-24} \text{ g}}{5 \times 10^{-40} \text{ cm}^3} = 3 \times 10^{15} \text{ g/cm}^3$$

Density of H atom (contains one proton and one electron):

$$V_{\text{atom}} = \frac{4}{3} (3.14) (1 \times 10^{-8} \text{ cm})^3 = 4 \times 10^{-24} \text{ cm}^3$$

$$d = \frac{1.67 \times 10^{-24} \text{ g} + 9 \times 10^{-28} \text{ g}}{4 \times 10^{-24} \text{ cm}^3} = 0.4 \text{ g/cm}^3$$

34. Because electrons move about the nucleus at an average distance of about 1×10^{-8} cm, the diameter of an atom will be about 2×10^{-8} cm. Let's set up a ratio:

$$\frac{\text{diameter of nucleus}}{\text{diameter of atom}} = \frac{1 \text{ mm}}{\text{diameter of model}} = \frac{1 \times 10^{-13} \text{ cm}}{2 \times 10^{-8} \text{ cm}}; \text{ solving:}$$

$$\text{diameter of model} = 2 \times 10^5 \text{ mm} = 200 \text{ m}$$

35. $3 \times 5.93 \times 10^{-18} \text{ C} \times \frac{1 \text{ electron charge}}{1.602 \times 10^{-19} \text{ C}} = 37$ negative (electron) charges on the oil drop

36. First, divide all charges by the smallest quantity, 6.40×10^{-13} :

$$\frac{2.56 \times 10^{-12}}{6.40 \times 10^{-13}} = 4.00; \quad \frac{7.68}{0.640} = 12.0; \quad \frac{3.84}{0.640} = 6.00$$

Because all charges are whole-number multiples of 6.40×10^{-13} zirkombs, the charge on one electron could be 6.40×10^{-13} zirkombs. However, 6.40×10^{-13} zirkombs could be the charge of two electrons (or three electrons, etc.). All one can conclude is that the charge of an electron is 6.40×10^{-13} zirkombs or an integer fraction of 6.40×10^{-13} zirkombs.

37. Z is the atomic number and is equal to the number of protons in the nucleus. A is the mass number and is equal to the number of protons plus neutrons in the nucleus. X is the symbol of the element. See the front cover of the text which has a listing of the symbols for the various elements and corresponding atomic number or see the periodic table on the cover to determine the identity of the various atoms. Because all of the atoms have equal numbers of protons and electrons, each atom is neutral in charge.
- a. ${}_{11}^{23}\text{Na}$ b. ${}_{9}^{19}\text{F}$ c. ${}_{8}^{16}\text{O}$
38. The atomic number for carbon is 6. ${}^{14}\text{C}$ has 6 protons, $14 - 6 = 8$ neutrons, and 6 electrons in the neutral atom. ${}^{12}\text{C}$ has 6 protons, $12 - 6 = 6$ neutrons, and 6 electrons in the neutral atom. The only difference between an atom of ${}^{14}\text{C}$ and an atom of ${}^{12}\text{C}$ is that ${}^{14}\text{C}$ has two additional neutrons.
39. a. ${}_{35}^{79}\text{Br}$: 35 protons, $79 - 35 = 44$ neutrons. Because the charge of the atom is neutral, the number of protons = the number of electrons = 35.
- b. ${}_{35}^{81}\text{Br}$: 35 protons, 46 neutrons, 35 electrons
- c. ${}_{94}^{239}\text{Pu}$: 94 protons, 145 neutrons, 94 electrons
- d. ${}_{55}^{133}\text{Cs}$: 55 protons, 78 neutrons, 55 electrons
- e. ${}_{1}^3\text{H}$: 1 proton, 2 neutrons, 1 electron
- f. ${}_{26}^{56}\text{Fe}$: 26 protons, 30 neutrons, 26 electrons
40. a. ${}_{92}^{235}\text{U}$: 92 p, 143 n, 92 e b. ${}_{13}^{27}\text{Al}$: 13 p, 14 n, 13 e c. ${}_{26}^{57}\text{Fe}$: 26 p, 31 n, 26 e
- d. ${}_{82}^{208}\text{Pb}$: 82 p, 126 n, 82 e e. ${}_{37}^{86}\text{Rb}$: 37 p, 49 n, 37 e f. ${}_{20}^{41}\text{Ca}$: 20 p, 21 n, 20 e
41. a. Element 8 is oxygen. $A = \text{mass number} = 9 + 8 = 17$; ${}_{8}^{17}\text{O}$
- b. Chlorine is element 17. ${}_{17}^{37}\text{Cl}$ c. Cobalt is element 27. ${}_{27}^{60}\text{Co}$
- d. $Z = 26$; $A = 26 + 31 = 57$; ${}_{26}^{57}\text{Fe}$ e. Iodine is element 53. ${}_{53}^{131}\text{I}$
- f. Lithium is element 3. ${}_{3}^7\text{Li}$

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42. a. Cobalt is element 27. $A = \text{mass number} = 27 + 31 = 58$; ${}_{27}^{58}\text{Co}$
- b. ${}_{5}^{10}\text{B}$ c. ${}_{12}^{23}\text{Mg}$ d. ${}_{53}^{132}\text{I}$ e. ${}_{20}^{47}\text{Ca}$ f. ${}_{29}^{65}\text{Cu}$
43. a. Ba is element 56. Ba^{2+} has 56 protons, so Ba^{2+} must have 54 electrons in order to have a net charge of $2+$.
- b. Zn is element 30. Zn^{2+} has 30 protons and 28 electrons.
- c. N is element 7. N^{3-} has 7 protons and 10 electrons.
- d. Rb is element 37, Rb^{+} has 37 protons and 36 electrons.
- e. Co is element 27. Co^{3+} has 27 protons and 24 electrons.
- f. Te is element 52. Te^{2-} has 52 protons and 54 electrons.
- g. Br is element 35. Br^{-} has 35 protons and 36 electrons.
44. a. ${}_{12}^{24}\text{Mg}$: 12 protons, 12 neutrons, 12 electrons
- b. ${}_{12}^{24}\text{Mg}^{2+}$: 12 p, 12 n, 10 e c. ${}_{27}^{59}\text{Co}^{2+}$: 27 p, 32 n, 25 e
- d. ${}_{27}^{59}\text{Co}^{3+}$: 27 p, 32 n, 24 e e. ${}_{27}^{59}\text{Co}$: 27 p, 32 n, 27 e
- f. ${}_{34}^{79}\text{Se}$: 34 p, 45 n, 34 e g. ${}_{34}^{79}\text{Se}^{2-}$: 34 p, 45 n, 36 e
- h. ${}_{28}^{63}\text{Ni}$: 28 p, 35 n, 28 e i. ${}_{28}^{59}\text{Ni}^{2+}$: 28 p, 31 n, 26 e
45. Atomic number = 63 (Eu); net charge = $+63 - 60 = 3+$; mass number = $63 + 88 = 151$; symbol: ${}_{63}^{151}\text{Eu}^{3+}$
- Atomic number = 50 (Sn); mass number = $50 + 68 = 118$; net charge = $+50 - 48 = 2+$;
symbol: ${}_{50}^{118}\text{Sn}^{2+}$
46. Atomic number = 16 (S); net charge = $+16 - 18 = 2-$; mass number = $16 + 18 = 34$; symbol: ${}_{16}^{34}\text{S}^{2-}$
- Atomic number = 16 (S); net charge = $+16 - 18 = 2-$; mass number = $16 + 16 = 32$;
symbol: ${}_{16}^{32}\text{S}^{2-}$

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47.

Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons	Net charge
${}_{92}^{238}\text{U}$	92	146	92	0
${}_{20}^{40}\text{Ca}^{2+}$	20	20	18	2+
${}_{23}^{51}\text{V}^{3+}$	23	28	20	3+
${}_{39}^{89}\text{Y}$	39	50	39	0
${}_{35}^{79}\text{Br}^{-}$	35	44	36	1-
${}_{15}^{31}\text{P}^{3-}$	15	16	18	3-

48.

Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons	Net charge
${}_{26}^{53}\text{Fe}^{2+}$	26	27	24	2+
${}_{26}^{59}\text{Fe}^{3+}$	26	33	23	3+
${}_{85}^{210}\text{At}^{-}$	85	125	86	1-
${}_{13}^{27}\text{Al}^{3+}$	13	14	10	3+
${}_{52}^{128}\text{Te}^{2-}$	52	76	54	2-

Chem Work Problems

49.

Number of protons in nucleus	Number of neutrons in nucleus	Symbol
9	10	${}^{19}_9\text{F}$
13	14	${}^{27}_{13}\text{Al}$
53	74	${}^{127}_{53}\text{I}$
34	45	${}^{79}_{34}\text{Se}$
16	16	${}^{32}_{16}\text{S}$

50.

Symbol	Number of protons in nucleus	Number of neutrons in nucleus
${}^4_2\text{He}$	2	2
${}^{20}_{10}\text{Ne}$	10	10
${}^{48}_{22}\text{Ti}$	22	26
${}^{190}_{76}\text{Os}$	76	114
${}^{50}_{27}\text{Co}$	27	23

51. ${}^{53}_{26}\text{Fe}^{2+}$ has 26 protons, $53 - 26 = 27$ neutrons, and two fewer electrons than protons (24 electrons) in order to have a net charge of $2+$.

52.

Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons
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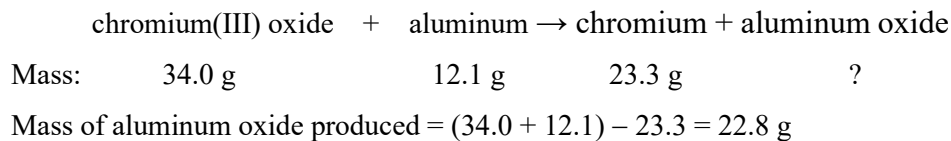
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${}_{50}^{120}\text{Sn}$	50	70	50
${}_{12}^{25}\text{Mg}^{2+}$	12	13	10
${}_{26}^{56}\text{Fe}^{2+}$	26	30	24
${}_{34}^{79}\text{Se}$	34	45	34
${}_{17}^{35}\text{Cl}$	17	18	17
${}_{29}^{63}\text{Cu}$	29	34	29

- 53.
- False. Neutrons have no charge; therefore, all particles in a nucleus are not charged.
 - False. The atom is best described as having a tiny dense nucleus containing most of the mass of the atom with the electrons moving about the nucleus at relatively large distances away; so much so that an atom is mostly empty space.
 - False. The mass of the nucleus makes up most of the mass of the entire atom.
 - True.
 - False. The number of protons in a neutral atom must equal the number of electrons.
54. a. True
- False; this was J. J. Thomson.
 - False; a proton is about 1800 times more massive than an electron.
 - The nucleus contains the protons and the neutrons.
55. For a 2- charge having 36 electrons, X^{2-} must have two fewer protons than electrons or 34 protons. This isotope of X has $79 - 34 = 45$ neutrons, and from the periodic table, X is selenium.
- True. X^{2-} has 36 electrons and 34 protons.
 - False. The isotope has 34 protons.
 - False. The isotope has 45 neutrons.
 - False. The identity is selenium, Se.
56. Because the charge of the ion is 2+, this ion has two more protons than electrons. Therefore, the element has 88 protons, which identifies it as radium, Ra. $230 - 88 = 142$ neutrons.

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57. Mass is conserved in a chemical reaction.



58. Number of electrons in the unknown ion:

$$2.55 \times 10^{-26} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ electron}}{9.11 \times 10^{-31} \text{ kg}} = 28 \text{ electrons}$$

Number of protons in the unknown ion:

$$5.34 \times 10^{-23} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ proton}}{1.67 \times 10^{-27} \text{ kg}} = 32 \text{ protons}$$

Therefore, this ion has 32 protons and 28 electrons. This is element number 32, germanium (Ge). The net charge is 4+ because four electrons have been lost from a neutral germanium atom.

The number of electrons in the unknown atom:

$$3.92 \times 10^{-26} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ electron}}{9.11 \times 10^{-31} \text{ kg}} = 43 \text{ electrons}$$

In a neutral atom, the number of protons and electrons is the same. Therefore, this is element 43, technetium (Tc).

The number of neutrons in the technetium atom:

$$9.35 \times 10^{-23} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ proton}}{1.67 \times 10^{-27} \text{ kg}} = 56 \text{ neutrons}$$

The mass number is the sum of the protons and neutrons. In this atom, the mass number is 43 protons + 56 neutrons = 99. Thus this atom and its mass number is ^{99}Tc .

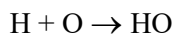
59. Most of the mass of the atom is due to the protons and the neutrons in the nucleus, and protons and neutrons have about the same mass ($1.67 \times 10^{-24} \text{ g}$). The ratio of the mass of the molecule to the mass of a nuclear particle will give a good approximation of the number of nuclear particles (protons and neutrons) present.

$$\frac{7.31 \times 10^{-23} \text{ g}}{1.67 \times 10^{-24} \text{ g}} = 43.8 \approx 44 \text{ nuclear particles}$$

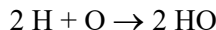
Thus there are 44 protons and neutrons present. If the number of protons equals the number of neutrons, we have 22 protons in the molecule. One possibility would be the molecule CO_2 [$6 + 2(8) = 22$ protons].

Challenge Problems

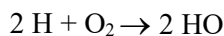
60. a. One possibility is that rope B is not attached to anything and rope A and rope C are connected via a pair of pulleys and/or gears.
- b. Try to pull rope B out of the box. Measure the distance moved by C for a given movement of A. Hold either A or C firmly while pulling on the other rope.
61. a. Both compounds have C_2H_6O as the formula. Because they have the same formula, their mass percent composition will be identical. However, these are different compounds with different properties because the atoms are bonded together differently. These compounds are called isomers of each other.
- b. When wood burns, most of the solid material in wood is converted to gases, which escape. The gases produced are most likely CO_2 and H_2O .
- c. The atom is not an indivisible particle but is instead composed of other smaller particles, called electrons, neutrons, and protons.
- d. The two hydride samples contain different isotopes of either hydrogen and/or lithium. Although the compounds are composed of different isotopes, their properties are similar because different isotopes of the same element have similar properties (except, of course, their mass).
62. Because the gases are at the same temperature and pressure, the volumes are directly proportional to the number of molecules present. Let's consider hydrogen and oxygen to be monatomic gases and that water has the simplest possible formula (HO). We have the equation:



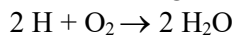
But the volume ratios are also equal to the molecule ratios, which correspond to the coefficients in the equation:



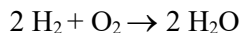
Because atoms cannot be created nor destroyed in a chemical reaction, this is not possible. To correct this, we can make oxygen a diatomic molecule:



This does not require hydrogen to be diatomic. Of course, if we know water has the formula H_2O , we get:



The only way to balance this is to make hydrogen diatomic:



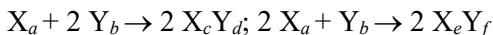
63. Avogadro proposed that equal volumes of gases (at constant temperature and pressure) contain equal numbers of molecules. In terms of balanced equations, Avogadro's hypothesis (law) implies that volume ratios will be identical to molecule ratios. Assuming one molecule of octane reacting, then 1 molecule of C_xH_y produces 8 molecules of CO_2 and 9 molecules of H_2O . $C_xH_y + n O_2 \rightarrow 8 CO_2 + 9 H_2O$. Because all the carbon in octane ends up as carbon in CO_2 , octane must contain 8 atoms of C. Similarly, all hydrogen in octane ends up as hydrogen in H_2O , so one molecule of octane must contain $9 \times 2 = 18$ atoms of H. Octane formula = C_8H_{18} , and the ratio of C : H = 8 : 18 or 4 : 9.
64. From Section 1-7 of the text, the average diameter of the nucleus is about 10^{-13} cm, and the electrons move about the nucleus at an average distance of about 10^{-8} cm. From this, the diameter of an atom is about 2×10^{-8} cm.

$$\frac{2 \times 10^{-8} \text{ cm}}{1 \times 10^{-13} \text{ cm}} = 2 \times 10^5; \quad \frac{1 \text{ mi}}{1 \text{ grape}} = \frac{5280 \text{ ft}}{1 \text{ grape}} = \frac{63,360 \text{ in}}{1 \text{ grape}}$$

Because the grape needs to be 2×10^5 times smaller than a mile, the diameter of the grape would need to be $63,360 / (2 \times 10^5) \approx 0.3$ in. This is a reasonable size for a small grape.

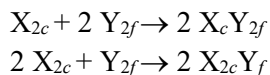
65. Let X_a be the formula for the atom/molecule X, Y_b be the formula for the atom/molecule Y, X_cY_d be the formula of compound I between X and Y, and X_eY_f be the formula of compound

II between X and Y. Using the volume data, the following would be the balanced equations for the production of the two compounds.

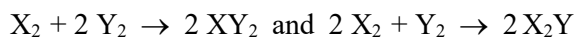


From the balanced equations, $a = 2c = e$ and $b = d = 2f$.

Substituting into the balanced equations:



For simplest formulas, assume that $c = f = 1$. Thus:



Compound I = XY_2 : If X has relative mass of 1.00, $\frac{1.00}{1.00 + 2y} = 0.3043$, $y = 1.14$.

Compound II = X_2Y : If X has relative mass of 1.00, $\frac{2.00}{2.00 + y} = 0.6364$, $y = 1.14$.

The relative mass of Y is 1.14 times that of X. Thus, if X has an atomic mass of 100, then Y will have an atomic mass of 114.

Marathon Problem

66. a. For each set of data, divide the larger number by the smaller number to determine relative masses.

$$\frac{0.602}{0.295} = 2.04; A = 2.04 \text{ when } B = 1.00$$

$$\frac{0.401}{0.172} = 2.33; C = 2.33 \text{ when } B = 1.00$$

$$\frac{0.374}{0.320} = 1.17; C = 1.17 \text{ when } A = 1.00$$

To have whole numbers, multiply the results by 3.

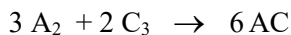
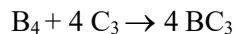
Data set 1: A = 6.1 and B = 3.0

Data set 2: C = 7.0 and B = 3.0

Data set 3: C = 3.5 and A = 3.0 or C = 7.0 and A = 6.0

Assuming 6.0 for the relative mass of A, the relative masses would be A = 6.0, B = 3.0, and C = 7.0 (if simplest formulas are assumed).

- b. Gas volumes are proportional to the number of molecules present. There are many possible correct answers for the balanced equations. One such solution that fits the gas volume data is:



In any correct set of reactions, the calculated mass data must match the mass data given initially in the problem. Here, the new table of relative masses would be:

$$\frac{6(\text{mass } A_2)}{\text{mass } B_4} = \frac{0.602}{0.295}; \text{mass } A_2 = 0.340(\text{mass } B_4)$$

$$\frac{4(\text{mass } C_3)}{\text{mass } B_4} = \frac{0.401}{0.172}; \text{mass } C_3 = 0.583(\text{mass } B_4)$$

$$\frac{2(\text{mass } C_3)}{3(\text{mass } A_2)} = \frac{0.374}{0.320}; \text{mass } A_2 = 0.570(\text{mass } C_3)$$

Assume some relative mass number for any of the masses. We will assume that mass B = 3.0, so mass B₄ = 4(3.0) = 12.

Mass C₃ = 0.583(12) = 7.0, mass C = 7.0/3

Mass A₂ = 0.570(7.0) = 4.0, mass A = 4.0/2 = 2.0

When we assume a relative mass for B = 3.0, then A = 2.0 and C = 7.0/3. The relative masses having all whole numbers would be A = 6.0, B = 9.0, and C = 7.0.

Note that any set of balanced reactions that confirms the initial mass data is correct. This is just one possibility.

CHAPTER 2

ATOMIC STRUCTURE AND PERIODICITY

Questions

19. The equations relating the terms are $v\lambda = c$, $E = hv$, and $E = hc/\lambda$. From the equations, wavelength and frequency are inversely related, photon energy and frequency are directly related, and photon energy and wavelength are inversely related. The unit of 1 Joule (J) = 1 kg m²/s². This is why you must change mass units to kg when using the deBroglie equation.
20. Frequency is the number of waves (cycles) of electromagnetic radiation per second that pass a given point in space. Speed refers to the distance a wave travels per unit time. All electromagnetic radiation (EMR) travels at the same speed (c, the speed of light = 2.998×10^8 m/s). However, each wavelength of EMR has its own unique frequency.
21. The photoelectric effect refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes it. The light must have a certain minimum frequency (energy) in order to remove electrons from the surface of a metal. Light having a frequency below the minimum results in no electrons being emitted, whereas light at or higher than the minimum frequency does cause electrons to be emitted. For light having a frequency higher than the minimum frequency, the excess energy is transferred into kinetic energy for the emitted electron. Albert Einstein explained the photoelectric effect by applying quantum theory.
22. The emission of light by excited atoms has been the key interconnection between the macroscopic world we can observe and measure, and what is happening on a microscopic basis within an atom. Excited atoms emit light (which we can observe and measure) because of changes in the microscopic structure of the atom. By studying the emissions of atoms, we can trace back to what happened inside the atom. Specifically, our current model of the atom relates the energy of light emitted to electrons in the atom moving from higher allowed energy states to lower allowed energy states.
23. Example 2-3 calculates the de Broglie wavelength of a ball and of an electron. The ball has a wavelength on the order of 10^{-34} m. This is incredibly short and, as far as the wave-particle duality is concerned, the wave properties of large objects are insignificant. The electron, with its tiny mass, also has a short wavelength; on the order of 10^{-10} m. However, this wavelength is significant because it is on the same order as the spacing between atoms in a typical crystal. For very tiny objects like electrons, the wave properties are important. The wave properties must be considered, along with the particle properties, when hypothesizing about the electron motion in an atom.

24. a. For hydrogen ($Z = 1$), the energy levels in units of Joules are given by the equation $E_n = -2.178 \times 10^{-18}(1/n^2)$. As n increases, the differences between $1/n^2$ for consecutive energy levels becomes smaller and smaller. Consider the difference between $1/n^2$ values for $n = 1$ and $n = 2$ as compared to $n = 3$ and $n = 4$.

For $n = 1$ and $n = 2$:

$$\frac{1}{1^2} - \frac{1}{2^2} = 1 - 0.25 = 0.75$$

For $n = 3$ and $n = 4$:

$$\frac{1}{3^2} - \frac{1}{4^2} = 0.1111 - 0.0625 = 0.0486$$

So because the differences between $1/n^2$ values for consecutive energy levels decrease as n increases, the energy levels get closer together as n increases.

- b. For a spectral transition for hydrogen, $\Delta E = E_f - E_i$:

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_i and n_f are the levels of the initial and final states, respectively. A positive value of ΔE always corresponds to an absorption of light, and a negative value of ΔE always corresponds to an emission of light.

In the diagram, the red line is for the $n_i = 3$ to $n_f = 2$ transition.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4} - \frac{1}{9} \right)$$

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \times (0.2500 - 0.1111) = -3.025 \times 10^{-19} \text{ J}$$

The photon of light must have precisely this energy ($3.025 \times 10^{-19} \text{ J}$).

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.025 \times 10^{-19} \text{ J}} \\ = 6.567 \times 10^{-7} \text{ m} = 656.7 \text{ nm}$$

From Figure 2-2, $\lambda = 656.7 \text{ nm}$ is red light so the diagram is correct for the red line.

In the diagram, the green line is for the $n_i = 4$ to $n_f = 2$ transition.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = -4.084 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.084 \times 10^{-19} \text{ J}} = 4.864 \times 10^{-7} \text{ m} = 486.4 \text{ nm}$$

From Figure 2-2, $\lambda = 486.4 \text{ nm}$ is green-blue light. So the diagram is ok with this line.

In the diagram, the blue line is for the $n_i = 5$ to $n_f = 2$ transition.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = -4.574 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.574 \times 10^{-19} \text{ J}} = 4.343 \times 10^{-7} \text{ m} = 434.3 \text{ nm}$$

From Figure 2-2, $\lambda = 434.3 \text{ nm}$ is blue or blue-violet light. So the diagram is ok with this line also.

25. The Bohr model was an important step in the development of the current quantum mechanical model of the atom. The idea that electrons can only occupy certain, allowed energy levels is illustrated nicely (and relatively easily). We talk about the Bohr model to present the idea of quantized energy levels.
26. The figure on the left tells us that the probability of finding the electron in the 1s orbital at points along a line drawn outward in any direction. This probability is greatest close to the nucleus and drops off rapidly as the distance from the nucleus increases.
- The figure on the right represents the total probability of finding the electron at a particular distance from the nucleus for a 1s hydrogen orbital. For this distribution, the hydrogen 1s orbital is divided into successive thin spherical shells and the total probability of finding the electron in each spherical shell is plotted versus distance from the nucleus. This graph is called the radial probability distribution.
27. When the p and d orbital functions are evaluated at various points in space, the results sometimes have positive values and sometimes have negative values. The term phase is often associated with the + and - signs. For example, a sine wave has alternating positive and negative phases. This is analogous to the positive and negative values (phases) in the p and d orbitals.
28. The widths of the various blocks in the periodic table are determined by the number of electrons that can occupy the specific orbital(s). In the s block, we have one orbital ($\ell = 0$, $m_\ell = 0$) that can hold two electrons; the s block is two elements wide. For the f block, there are 7 degenerate f orbitals ($\ell = 3$, $m_\ell = -3, -2, -1, 0, 1, 2, 3$), so the f block is 14 elements wide. The g block corresponds to $\ell = 4$. The number of degenerate g orbitals is 9. This comes from the 9 possible m_ℓ values when $\ell = 4$ ($m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$). With 9 orbitals, each orbital holding two electrons, the g block would be 18 elements wide. The h block has $\ell = 5$, $m_\ell = -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5$. With 11 degenerate h orbitals, the h block would be 22 elements wide.
29. If one more electron is added to a half-filled subshell, electron-electron repulsions will increase because two electrons must now occupy the same atomic orbital. This may slightly decrease the stability of the atom.
30. Size decreases from left to right and increases going down the periodic table. Thus, going one element right and one element down would result in a similar size for the two elements diagonal to each other. The ionization energies will be similar for the diagonal elements since the periodic trends also oppose each other. Electron affinities are harder to predict, but atoms with similar sizes and ionization energies should also have similar electron affinities.

31. Electron-electron repulsions become more important when we try to add electrons to an atom. From the standpoint of electron-electron repulsions, larger atoms would have more favorable (more negative) electron affinities. Considering only electron-nucleus attractions, smaller atoms would be expected to have the more favorable (more negative) electron affinity values. These trends are exactly the opposite of each other. Thus the overall variation in electron affinity is not as great as ionization energy in which attractions to the nucleus dominate.
32. For hydrogen and one-electron ions (hydrogen-like ions), all atomic orbitals with the same ℓ value have the same energy. For polyatomic atoms/ions, the energy of the atomic orbitals also depends on ℓ . Because there are more nondegenerate energy levels for polyatomic atoms/ions as compared to hydrogen, there are many more possible electronic transitions resulting in more complicated line spectra.
33. Each element has a characteristic spectrum because each element has unique energy levels. Thus the presence of the characteristic spectral lines of an element confirms its presence in any particular sample.
34. Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron-electron repulsions.
35. The electron is no longer part of that atom. The proton and electron are completely separated.
36. Ionization energy applies to the removal of the electron from an atom in the gas phase. The work function applies to the removal of an electron from the solid element.
Ionization energy: $M(g) \rightarrow M^+(g) + e^-$; work function: $M(s) \rightarrow M^+(s) + e^-$
37. Li^+ ions are the smallest of the alkali metal cations and will be most strongly attracted to the water molecules.

Exercises

Light and Matter

$$38. \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{780. \times 10^{-9} \text{ m}} = 3.84 \times 10^{14} \text{ s}^{-1}$$

$$39. 99.5 \text{ MHz} = 99.5 \times 10^6 \text{ Hz} = 99.5 \times 10^6 \quad ; \quad \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{99.5 \times 10^6 \text{ s}^{-1}} = 3.01 \text{ m}$$

$$40. \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.0 \times 10^{-2} \text{ m}} = 3.0 \times 10^{10}$$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J s} \times 3.0 \times 10^{10} = 2.0 \times 10^{-23} \text{ J/photon}$$

$$41. E = hv = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}}{25 \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 8.0 \times 10^{-18} \text{ J/photon}$$

$$\frac{8.0 \times 10^{-18} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} = 4.8 \times 10^6 \text{ J/mol}$$

$$42. \quad 280 \text{ nm: } \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{280 \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 1.1 \times 10^{15}$$

$$320 \text{ nm: } \nu = \frac{3.00 \times 10^8 \text{ m/s}}{320 \times 10^{-9} \text{ nm}} = 9.4 \times 10^{14}$$

The compounds in the sunscreen absorb ultraviolet B (UVB) electromagnetic radiation having a frequency from 9.4×10^{14} to 1.1×10^{15} .

$$43. \quad \text{S-type cone receptors: } \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{6.00 \times 10^{14} \text{ s}^{-1}} = 5.00 \times 10^{-7} \text{ m} = 500. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{7.49 \times 10^{14} \text{ s}^{-1}} = 4.00 \times 10^{-7} \text{ m} = 400. \text{ nm}$$

S-type cone receptors detect 400-500 nm light. From Figure 2-2 in the text, this is violet to green light.

$$\text{M-type cone receptors: } \lambda = \frac{2.998 \times 10^8 \text{ m/s}}{4.76 \times 10^{14} \text{ s}^{-1}} = 6.30 \times 10^{-7} \text{ m} = 630. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{6.62 \times 10^{14} \text{ s}^{-1}} = 4.53 \times 10^{-7} \text{ m} = 453 \text{ nm}$$

M-type cone receptors detect 450-630 nm light. From Figure 2-2 in the text, this is blue to orange light.

$$\text{L-type cone receptors: } \lambda = \frac{2.998 \times 10^8 \text{ m/s}}{4.28 \times 10^{14} \text{ s}^{-1}} = 7.00 \times 10^{-7} \text{ m} = 700. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{6.00 \times 10^{14} \text{ s}^{-1}} = 5.00 \times 10^{-7} \text{ m} = 500. \text{ nm}$$

L-type cone receptors detect 500-700 nm light. This represents green to red light.

44. The wavelength is the distance between consecutive wave peaks. Wave *a* shows 4 wavelengths, and wave *b* shows 8 wavelengths.

$$\text{Wave } a: \lambda = \frac{1.6 \times 10^{-3} \text{ m}}{4} = 4.0 \times 10^{-4} \text{ m}$$

$$\text{Wave } b: \lambda = \frac{1.6 \times 10^{-3} \text{ m}}{8} = 2.0 \times 10^{-4} \text{ m}$$

Wave *a* has the longer wavelength. Because frequency and photon energy are both inversely proportional to wavelength, wave *b* will have the higher frequency and larger photon energy since it has the shorter wavelength.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 1.5 \times 10^{12} \text{ s}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 9.9 \times 10^{-22} \text{ J}$$

Because both waves are examples of electromagnetic radiation, both waves travel at the same speed, *c*, the speed of light. From Figure 2-2 of the text, both of these waves represent infrared electromagnetic radiation.

45. Referencing Figure 2-2 of the text, $2.12 \times 10^{-10} \text{ m}$ electromagnetic radiation is X rays.

$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{107.1 \times 10^6 \text{ s}^{-1}} = 2.799 \text{ m}$$

From the wavelength calculated above, 107.1 MHz electromagnetic radiation is FM radio-waves.

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{3.97 \times 10^{-19} \text{ J}} = 5.00 \times 10^{-7} \text{ m}$$

The $3.97 \times 10^{-19} \text{ J}$ /photon electromagnetic radiation is visible (green) light.

The photon energy and frequency order will be the exact opposite of the wavelength ordering because *E* and ν are both inversely related to λ . From the previously calculated wavelengths, the order of photon energy and frequency is:

FM radiowaves	<	visible (green) light	<	X rays
longest λ				shortest λ
lowest ν				highest ν
smallest <i>E</i>				largest <i>E</i>

46.
$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{150. \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 1.32 \times 10^{-18} \text{ J}$$

$$1.98 \times 10^5 \text{ J} \times \frac{1 \text{ photon}}{1.32 \times 10^{-18} \text{ J}} \times \frac{1 \text{ atom C}}{\text{photon}} = 1.50 \times 10^{23} \text{ atoms C}$$

$$47. \quad E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad E_{\text{photon}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{1.0 \times 10^{-10} \text{ m}} = 2.0 \times 10^{-15} \text{ J}$$

$$\frac{2.0 \times 10^{-15} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.2 \times 10^6 \text{ kJ/mol}$$

$$E_{\text{photon}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{1.0 \times 10^4 \text{ m}} = 2.0 \times 10^{-29} \text{ J}$$

$$\frac{2.0 \times 10^{-29} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.2 \times 10^{-8} \text{ kJ/mol}$$

X rays do have an energy greater than the carbon-carbon bond energy. Therefore, X rays could conceivably break carbon-carbon bonds in organic compounds and thereby disrupt the function of an organic molecule. Radio waves, however, do not have sufficient energy to break carbon-carbon bonds and are therefore relatively harmless.

48. The energy needed to remove a single electron is:

$$\frac{279.7 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 4.645 \times 10^{-22} \text{ kJ} = 4.645 \times 10^{-19} \text{ J}$$

$$E = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.645 \times 10^{-19} \text{ J}} = 4.277 \times 10^{-7} \text{ m} = 427.7 \text{ nm}$$

$$49. \quad \frac{208.4 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 3.461 \times 10^{-22} \text{ kJ} = 3.461 \times 10^{-19} \text{ J to remove one electron}$$

$$E = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.461 \times 10^{-19} \text{ J}} = 5.739 \times 10^{-7} \text{ m} = 573.9 \text{ nm}$$

50. Ionization energy = energy to remove an electron = $7.21 \times 10^{-19} \text{ J} = E_{\text{photon}}$

$$E_{\text{photon}} = h\nu \text{ and } \lambda\nu = c. \text{ So } \nu = \frac{c}{\lambda} \text{ and } E = \frac{hc}{\lambda}.$$

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{7.21 \times 10^{-19} \text{ J}} = 2.76 \times 10^{-7} \text{ m} = 276 \text{ nm}$$

$$51. \quad \frac{890.1 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = \frac{1.478 \times 10^{-21} \text{ kJ}}{\text{atom}} = \frac{1.478 \times 10^{-18} \text{ J}}{\text{atom}}$$

= ionization energy per atom

CHAPTER 2 ATOMIC STRUCTURE AND PERIODICITY

$$E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.478 \times 10^{-18} \text{ J}} = 1.344 \times 10^{-7} \text{ m} = 134.4 \text{ nm}$$

No, it will take light having a wavelength of 134.4 nm or less to ionize gold. A photon of light having a wavelength of 225 nm is longer wavelength and thus lower energy than 134.4 nm light.

52. a. 10.% of speed of light = $0.10 \times 3.00 \times 10^8 \text{ m/s} = 3.0 \times 10^7 \text{ m/s}$

$$\lambda = \frac{h}{mv}, \lambda = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 3.0 \times 10^7 \text{ m/s}} = 2.4 \times 10^{-11} \text{ m} = 2.4 \times 10^{-2} \text{ nm}$$

Note: For units to come out, the mass must be in kg because $1 \text{ J} = \frac{1 \text{ kg m}^2}{\text{s}^2}$.

b. $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{0.055 \text{ kg} \times 35 \text{ m/s}} = 3.4 \times 10^{-34} \text{ m} = 3.4 \times 10^{-25} \text{ nm}$

This number is so small that it is insignificant. We cannot detect a wavelength this small. The meaning of this number is that we do not have to worry about the wave properties of large objects.

53. a. $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{1.675 \times 10^{-27} \text{ kg} \times (0.0100 \times 2.998 \times 10^8 \text{ m/s})} = 1.32 \times 10^{-13} \text{ m}$

b. $\lambda = \frac{h}{mv}, v = \frac{h}{\lambda m} = \frac{6.626 \times 10^{-34} \text{ J s}}{75 \times 10^{-12} \text{ m} \times 1.675 \times 10^{-27} \text{ kg}} = 5.3 \times 10^3 \text{ m/s}$

54. $\lambda = \frac{h}{mv}, m = \frac{h}{\lambda v} = \frac{6.63 \times 10^{-34} \text{ J s}}{1.5 \times 10^{-15} \text{ m} \times (0.90 \times 3.00 \times 10^8 \text{ m/s})} = 1.6 \times 10^{-27} \text{ kg}$

This particle is probably a proton or a neutron.

55. $\lambda = \frac{h}{mv}, v = \frac{h}{\lambda m};$ for $\lambda = 1.0 \times 10^2 \text{ nm} = 1.0 \times 10^{-7} \text{ m}:$

$$v = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 1.0 \times 10^{-7} \text{ m}} = 7.3 \times 10^3 \text{ m/s}$$

For $\lambda = 1.0 \text{ nm} = 1.0 \times 10^{-9} \text{ m}:$ $v = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 1.0 \times 10^{-9} \text{ m}} = 7.3 \times 10^5 \text{ m/s}$

Hydrogen Atom: The Bohr Model

56. For the H atom ($Z = 1$): $E_n = -2.178 \times 10^{-18} \text{ J}/n^2$; for a spectral transition, $\Delta E = E_f - E_i$:

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_i and n_f are the levels of the initial and final states, respectively. A positive value of ΔE always corresponds to an absorption of light, and a negative value of ΔE always corresponds to an emission of light.

$$\text{a. } \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4} - \frac{1}{9} \right)$$

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \times (0.2500 - 0.1111) = -3.025 \times 10^{-19} \text{ J}$$

The photon of light must have precisely this energy ($3.025 \times 10^{-19} \text{ J}$).

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.025 \times 10^{-19} \text{ J}} \\ = 6.567 \times 10^{-7} \text{ m} = 656.7 \text{ nm}$$

From Figure 2-2, this is visible electromagnetic radiation (red light).

$$\text{b. } \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = -4.084 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.084 \times 10^{-19} \text{ J}} = 4.864 \times 10^{-7} \text{ m} = 486.4 \text{ nm}$$

This is visible electromagnetic radiation (green-blue light).

$$\text{c. } \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = -1.634 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm}$$

This is ultraviolet electromagnetic radiation.

$$\text{57. a. } \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = -1.059 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.059 \times 10^{-19} \text{ J}} = 1.876 \times 10^{-6} \text{ m} = 1876 \text{ nm}$$

From Figure 2-2, this is infrared electromagnetic radiation.

CHAPTER 2 ATOMIC STRUCTURE AND PERIODICITY

b. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = -4.901 \times 10^{-20} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.901 \times 10^{-20} \text{ J}} = 4.053 \times 10^{-6} \text{ m}$$

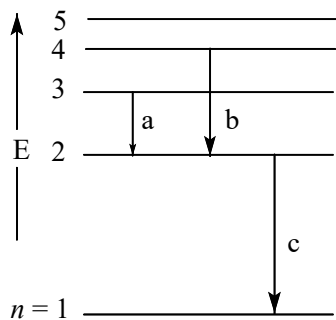
= 4053 nm (infrared)

c. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} - \frac{1}{5^2} \right) = -1.549 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.549 \times 10^{-19} \text{ J}} = 1.282 \times 10^{-6} \text{ m}$$

= 1282 nm (infrared)

58.



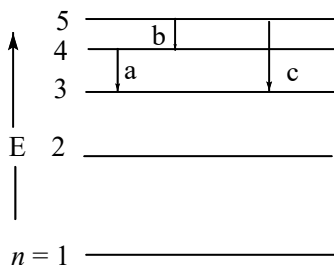
a. $3 \rightarrow 2$

b. $4 \rightarrow 2$

c. $2 \rightarrow 1$

Energy levels are not to scale.

59.



a. $4 \rightarrow 3$

b. $5 \rightarrow 4$

c. $5 \rightarrow 3$

Energy levels are not to scale.

60. The longest wavelength light emitted will correspond to the transition with the smallest energy change (smallest ΔE). This is the transition from $n = 6$ to $n = 5$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{6^2} \right) = -2.662 \times 10^{-20} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.662 \times 10^{-20} \text{ J}} = 7.462 \times 10^{-6} \text{ m} = 7462 \text{ nm}$$

The shortest wavelength emitted will correspond to the largest ΔE ; this is $n = 6 \rightarrow n = 1$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{6^2} \right) = -2.118 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.118 \times 10^{-18} \text{ J}} = 9.379 \times 10^{-8} \text{ m} = 93.79 \text{ nm}$$

61. There are 4 possible transitions for an electron in the $n = 5$ level ($5 \rightarrow 4$, $5 \rightarrow 3$, $5 \rightarrow 2$, and $5 \rightarrow 1$). If an electron initially drops to the $n = 4$ level, three additional transitions can occur ($4 \rightarrow 3$, $4 \rightarrow 2$, and $4 \rightarrow 1$). Similarly, there are two more transitions from the $n = 3$ level ($3 \rightarrow 2$, $3 \rightarrow 1$) and one more transition for the $n = 2$ level ($2 \rightarrow 1$). There are a total of 10 possible transitions for an electron in the $n = 5$ level for a possible total of 10 different wavelength emissions.

$$62. \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{1^2} \right) = 2.091 \times 10^{-18} \text{ J} = E_{\text{photon}}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.091 \times 10^{-18} \text{ J}} = 9.500 \times 10^{-8} \text{ m} = 95.00 \text{ nm}$$

Because wavelength and energy are inversely related, visible light ($\lambda \approx 400\text{--}700 \text{ nm}$) is not energetic enough to excite an electron in hydrogen from $n = 1$ to $n = 5$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{6^2} - \frac{1}{2^2} \right) = 4.840 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.840 \times 10^{-19} \text{ J}} = 4.104 \times 10^{-7} \text{ m} = 410.4 \text{ nm}$$

63. Visible light with $\lambda = 410.4 \text{ nm}$ will excite an electron from the $n = 2$ to the $n = 6$ energy level.
- False; it takes less energy to ionize an electron from $n = 3$ than from the ground state.
 - True
 - False; the energy difference between $n = 3$ and $n = 2$ is smaller than the energy difference between $n = 3$ and $n = 1$; thus the wavelength is larger for the $n = 3 \rightarrow n = 2$ electronic transition than for the $n = 3 \rightarrow n = 1$ transition. E and λ are inversely proportional to each other ($E = hc/\lambda$).
 - True
 - False; $n = 2$ is the first excited state, and $n = 3$ is the second excited state.

64. Ionization from $n = 1$ corresponds to the transition $n_i = 1 \rightarrow n_f = \infty$, where $E_\infty = 0$.

$$\Delta E = E_\infty - E_1 = -E_1 = 2.178 \times 10^{-18} \left(\frac{1}{1^2} \right) = 2.178 \times 10^{-18} \text{ J} = E_{\text{photon}}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.178 \times 10^{-18} \text{ J}} = 9.120 \times 10^{-8} \text{ m} = 91.20 \text{ nm}$$

To ionize from $n = 2$, $\Delta E = E_\infty - E_2 = -E_2 = 2.178 \times 10^{-18} \left(\frac{1}{2^2} \right) = 5.445 \times 10^{-19} \text{ J}$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{5.445 \times 10^{-19} \text{ J}} = 3.648 \times 10^{-7} \text{ m} = 364.8 \text{ nm}$$

65. $\Delta E = E_\infty - E_n = -E_n = 2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} \right)$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1460 \times 10^{-9} \text{ m}} = 1.36 \times 10^{-19} \text{ J}$$

$$E_{\text{photon}} = \Delta E = 1.36 \times 10^{-19} \text{ J} = 2.178 \times 10^{-18} \left(\frac{1}{n^2} \right), \quad n^2 = 16.0, \quad n = 4$$

66. $|\Delta E| = E_{\text{photon}} = h\nu = 6.662 \times 10^{-34} \text{ J s} \times 6.90 \times 10^{14} \text{ s}^{-1} = 4.57 \times 10^{-19} \text{ J}$

$\Delta E = -4.57 \times 10^{-19} \text{ J}$ because we have an emission.

$$-4.57 \times 10^{-19} \text{ J} = E_n - E_5 = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} - \frac{1}{5^2} \right)$$

$$\frac{1}{n^2} - \frac{1}{25} = 0.210, \quad \frac{1}{n^2} = 0.250, \quad n^2 = 4, \quad n = 2$$

The electronic transition is from $n = 5$ to $n = 2$.

67. $|\Delta E| = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{397.2 \times 10^{-9} \text{ m}} = 5.001 \times 10^{-19} \text{ J}$

$\Delta E = -5.001 \times 10^{-19} \text{ J}$ because we have an emission.

$$-5.001 \times 10^{-19} \text{ J} = E_2 - E_n = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

$$0.2296 = \frac{1}{4} - \frac{1}{n^2}, \quad \frac{1}{n^2} = 0.0204, \quad n = 7$$

Quantum Mechanics, Quantum Numbers, and Orbitals

68. a. $\Delta p = m\Delta v = 9.11 \times 10^{-31} \text{ kg} \times 0.100 \text{ m/s} = \frac{9.11 \times 10^{-32} \text{ kg m}}{\text{s}}$

$$\Delta p \Delta x \geq \frac{h}{4\pi}, \Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times (9.11 \times 10^{-32} \text{ kg m/s})} = 5.79 \times 10^{-4} \text{ m}$$

$$\text{b. } \Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times 0.145 \text{ kg} \times 0.100 \text{ m/s}} = 3.64 \times 10^{-33} \text{ m}$$

The diameter of an H atom is roughly 2×10^{-8} cm. The uncertainty in the position of the electron is much larger than the size of the atom, whereas, the uncertainty in the position of the baseball is insignificant as compared to the size of a baseball.

Units of $\Delta E \cdot \Delta t = \text{J} \times \text{s}$, the same as the units of Planck's constant.

$$\text{Units of } \Delta(mv) \cdot \Delta x = \text{kg} \times \frac{\text{m}}{\text{s}} \times \text{m} = \frac{\text{kg m}^2}{\text{s}} = \frac{\text{kg m}^2}{\text{s}^2} \times \text{s} = \text{J} \times \text{s}$$

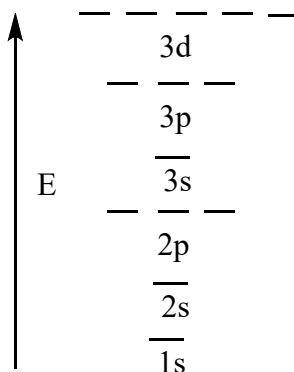
69. $n = 1, 2, 3, \dots$; $\ell = 0, 1, 2, \dots (n - 1)$; $m_\ell = -\ell \dots -2, -1, 0, 1, 2, \dots +\ell$
70. a. This general shape represents a p orbital ($\ell = 1$) and because there is a node in each of the lobes, this figure represents a 3p orbital ($n = 3, \ell = 1$)
- b. This is an s orbital ($\ell = 0$). And because there is one node present, this is a 2s orbital ($n = 2, \ell = 0$).
- c. This is the shape of a specific d oriented orbital ($\ell = 2$). This orbital is designated as a d_{z^2} . Because no additional nodes are present inside any of the boundary surfaces, this is a $3d_{z^2}$ orbital ($n = 3, \ell = 2$).
71. b. For $\ell = 3$, m_ℓ can range from -3 to $+3$; thus $+4$ is not allowed.
- c. n cannot equal zero. d. ℓ cannot be a negative number.
72. a. For $n = 3$, $\ell = 3$ is not possible.
- d. m_s cannot equal -1 .
- e. ℓ cannot be a negative number.
- f. For $\ell = 1$, m_ℓ cannot equal 2.

The quantum numbers in parts b and c are allowed.

73. ψ^2 gives the probability of finding the electron at that point.
74. The diagrams of the orbitals in the text give only 90% probabilities of where the electron may reside. We can never be 100% certain of the location of the electrons due to Heisenberg's uncertainty principle.

Polyelectronic Atoms

75. He: $1s^2$; Ne: $1s^22s^22p^6$; Ar: $1s^22s^22p^63s^23p^6$; each peak in the diagram corresponds to a subshell with different values of n . Corresponding subshells are closer to the nucleus for heavier elements because of the increased nuclear charge.
76. In polyelectronic atoms, the orbitals of a given principal quantum level are not degenerate. In polyelectronic atoms, the energy order of the $n = 1, 2,$ and 3 orbitals are (not to scale):



In general, the lower the n value for an orbital, the closer on average the electron can be to the nucleus, and the lower the energy. Within a specific n value orbital (like $2s$ vs. $2p$ or $3s$ vs. $3p$ vs. $3d$), it is generally true that $E_{ns} < E_{np} < E_{nd} < E_{nf}$.

To rationalize this order, we utilize the radial probability distributions. In the $2s$ and $2p$ distribution, notice that the $2s$ orbital has a small hump of electron density very near the nucleus. This indicates that an electron in the $2s$ orbital can be very close to the nucleus some of the time. The $2s$ electron penetrates to the nucleus more than a $2p$ electron, and with this penetration comes a lower overall energy for the $2s$ orbital as compared to the $2p$ orbital.

In the $n = 3$ radial probability distribution, the $3s$ electron has two humps of electron density very close to the nucleus, and the $3p$ orbital has one hump very close to the nucleus. The $3s$ orbital electron is most penetrating, with the $3p$ orbital electron the next most penetrating, followed by the least penetrating $3d$ orbital electron. The more penetrating the electron, the lower the overall energy. Hence the $3s$ orbital is lower energy than the $3p$ orbitals which is lower energy than the $3d$ orbitals.

77. $5p$: three orbitals $3d_{z^2}$: one orbital $4d$: five orbitals

$n = 5$: $\ell = 0$ (1 orbital), $\ell = 1$ (3 orbitals), $\ell = 2$ (5 orbitals), $\ell = 3$ (7 orbitals),
 $\ell = 4$ (9 orbitals); total for $n = 5$ is 25 orbitals.

$n = 4$: $\ell = 0$ (1), $\ell = 1$ (3), $\ell = 2$ (5), $\ell = 3$ (7); total for $n = 4$ is 16 orbitals.

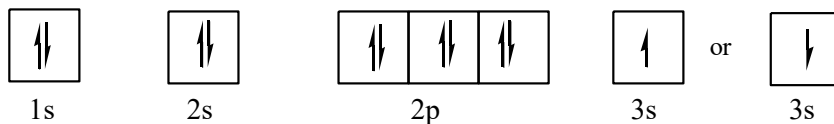
78. $1p$, 0 electrons ($\ell \neq 1$ when $n = 1$); $6d_{x^2-y^2}$, 2 electrons (specifies one atomic orbital); $4f$, 14 electrons (7 orbitals have $4f$ designation); $7p_y$, 2 electrons (specifies one atomic orbital); $2s$,

CHAPTER 2 ATOMIC STRUCTURE AND PERIODICITY

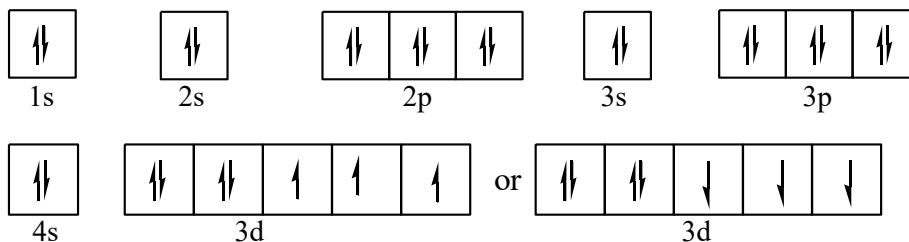
2 electrons (specifies one atomic orbital); $n = 3$, 18 electrons (3s, 3p, and 3d orbitals are possible; there are one 3s orbital, three 3p orbitals, and five 3d orbitals).

79. a. $n = 4$: ℓ can be 0, 1, 2, or 3. Thus we have s ($2 e^-$), p ($6 e^-$), d ($10 e^-$), and f ($14 e^-$) orbitals present. Total number of electrons to fill these orbitals is 32.
- b. $n = 5$, $m_\ell = +1$: For $n = 5$, $\ell = 0, 1, 2, 3, 4$. For $\ell = 1, 2, 3, 4$, all can have $m_\ell = +1$. Four distinct orbitals, thus 8 electrons.
- c. $n = 5$, $m_s = +1/2$: For $n = 5$, $\ell = 0, 1, 2, 3, 4$. Number of orbitals = 1, 3, 5, 7, 9 for each value of ℓ , respectively. There are 25 orbitals with $n = 5$. They can hold 50 electrons, and 25 of these electrons can have $m_s = +1/2$.
- d. $n = 3$, $\ell = 2$: These quantum numbers define a set of 3d orbitals. There are 5 degenerate 3d orbitals that can hold a total of 10 electrons.
- e. $n = 2$, $\ell = 1$: These define a set of 2p orbitals. There are 3 degenerate 2p orbitals that can hold a total of 6 electrons.
80. a. It is impossible to have $n = 0$. Thus no electrons can have this set of quantum numbers.
- b. The four quantum numbers completely specify a single electron in a 2p orbital.
- c. $n = 3$, $m_s = +1/2$: 3s, 3p, and 3d orbitals all have $n = 3$. These nine orbitals can each hold one electron with $m_s = +1/2$; 9 electrons can have these quantum numbers
- d. $n = 2$, $\ell = 2$: this combination is not possible ($\ell \neq 2$ for $n = 2$). Zero electrons in an atom can have these quantum numbers.
- e. $n = 1$, $\ell = 0$, $m_\ell = 0$: these define a 1s orbital that can hold 2 electrons.

81. a. Na: $1s^2 2s^2 2p^6 3s^1$; Na has 1 unpaired electron.

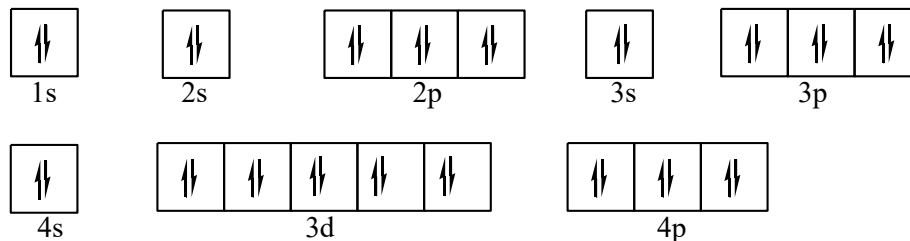


- b. Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$; Co has 3 unpaired electrons.



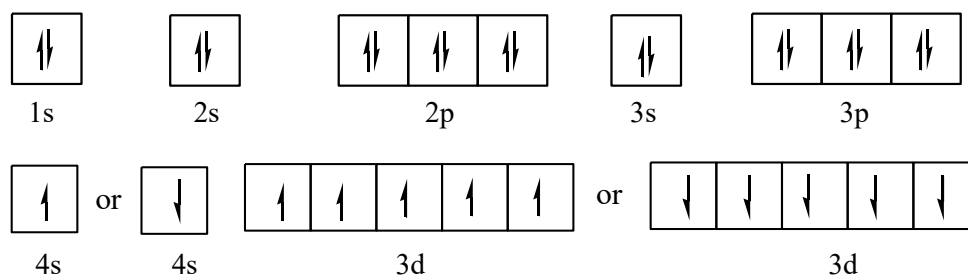
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c. Kr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$; Kr has 0 unpaired electrons.

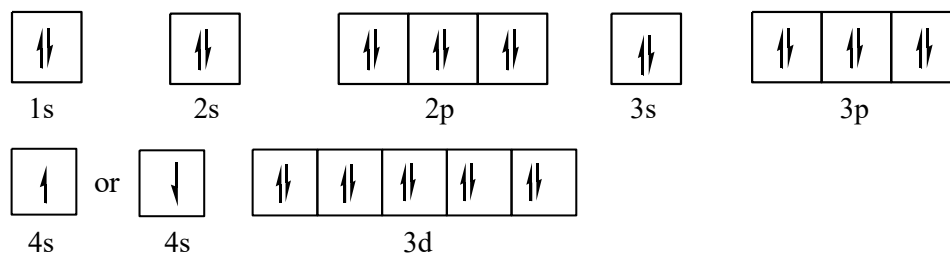


82. The two exceptions are Cr and Cu.

Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$; Cr has 6 unpaired electrons.



Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$; Cu has 1 unpaired electron.



83. Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ or $[\text{Ne}]3s^2 3p^2$; Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or $[\text{Ar}]4s^2 3d^{10} 4p^1$

As: $[\text{Ar}]4s^2 3d^{10} 4p^3$; Ge: $[\text{Ar}]4s^2 3d^{10} 4p^2$; Al: $[\text{Ne}]3s^2 3p^1$; Cd: $[\text{Kr}]5s^2 4d^{10}$

S: $[\text{Ne}]3s^2 3p^4$; Se: $[\text{Ar}]4s^2 3d^{10} 4p^4$

Cu: $[\text{Ar}]4s^2 3d^9$ (using periodic table), $[\text{Ar}]4s^1 3d^{10}$ (actual)

O: $1s^2 2s^2 2p^4$; La: $[\text{Xe}]6s^2 5d^1$; Y: $[\text{Kr}]5s^2 4d^1$; Ba: $[\text{Xe}]6s^2$

Tl: $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^1$; Bi: $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^3$

84. The following are complete electron configurations. Noble gas shorthand notation could also be used.

Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$; Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

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85. P: $1s^2 2s^2 2p^6 3s^2 3p^3$; Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$
 Eu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 5d^1$ *
 Pt: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$ *
 Xe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$; Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

*Note: These electron configurations were predicted using only the periodic table. The actual electron configurations are: Eu: $[\text{Xe}]6s^2 4f^7$ and Pt: $[\text{Xe}]6s^1 4f^{14} 5d^9$

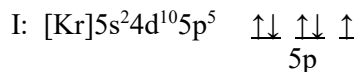
86. Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[\text{Ne}]3s^2 3p^5$ Sb: $[\text{Kr}]5s^2 4d^{10} 5p^3$
 Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$ or $[\text{Kr}]5s^2$ W: $[\text{Xe}]6s^2 4f^{14} 5d^4$
 Pb: $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^2$ Cf: $[\text{Rn}]7s^2 5f^{10}$ *

*Note: Predicting electron configurations for lanthanide and actinide elements is difficult since they have 0, 1, or 2 electrons in d orbitals. This is the actual Cf electron configuration.

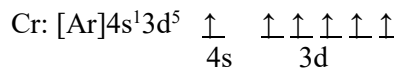
87. O: $1s^2 2s^2 2p^4$; C: $1s^2 2s^2 2p^2$; H: $1s^1$; N: $1s^2 2s^2 2p^3$; Ca: $[\text{Ar}]4s^2$; P: $[\text{Ne}]3s^2 3p^3$;
 Mg: $[\text{Ne}]3s^2$; K: $[\text{Ar}]4s^1$

88. Cr: $[\text{Ar}]4s^1 3d^5$, 6 unpaired electrons (Cr is an exception to the normal filling order);
 Mn: $[\text{Ar}]4s^2 3d^5$, 5 unpaired e^- ; Fe: $[\text{Ar}]4s^2 3d^6$, 4 unpaired e^- ; Co: $[\text{Ar}]4s^2 3d^7$, 3 unpaired e^- ;
 Ni: $[\text{Ar}]4s^2 3d^8$, 2 unpaired e^- ; Cu: $[\text{Ar}] 4s^1 3d^{10}$, 1 unpaired e^- (Cu is also an exception to the normal filling order); Zn: $[\text{Ar}]4s^2 3d^{10}$, 0 unpaired e^- .

89. a. Both In and I have one unpaired 5p electron, but only the nonmetal I would be expected to form a covalent compound with the nonmetal F. One would predict an ionic compound to form between the metal In and the nonmetal F.



- b. From the periodic table, this will be element 120. Element 120: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6 8s^2$
 c. Rn: $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^6$; note that the next discovered noble gas will also have 4f electrons (as well as 5f electrons).
 d. This is chromium, which is an exception to the predicted filling order. Cr has 6 unpaired electrons, and the next most is 5 unpaired electrons for Mn.



90. a. As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$
 b. Element 116 will be below Po in the periodic table: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^4$

- c. Ta: $[\text{Xe}]6s^24f^{14}5d^3$ or Ir: $[\text{Xe}]6s^24f^{14}5d^7$
- d. At: $[\text{Xe}]6s^24f^{14}5d^{10}6p^5$. Note that element 117 (when it is discovered) will also have electrons in the 6p atomic orbitals (as well as electrons in the 7p atomic orbitals).
91. a. The complete ground state electron for this neutral atom is $1s^22s^22p^63s^23p^4$. This atom has $2 + 2 + 6 + 2 + 4 = 16$ electrons. Because the atom is neutral, it also has 16 protons, making the atom sulfur, S.
- b. Complete excited state electron configuration: $1s^22s^12p^4$; this neutral atom has $2 + 1 + 4 = 7$ electrons, which means it has 7 protons, which identifies it as nitrogen, N.
- c. Complete ground state electron configuration: $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$; this 1- charged ion has 35 electrons. Because the overall charge is 1-, this ion has 34 protons which identifies it as selenium. The ion is Se^- .
92. a. This atom has 10 electrons. Ne b. S
- c. The predicted ground state configuration is $[\text{Kr}]5s^24d^9$. From the periodic table, the element is Ag. *Note:* $[\text{Kr}]5s^14d^{10}$ is the actual ground state electron configuration for Ag.
- d. Bi: $[\text{Xe}]6s^24f^{14}5d^{10}6p^3$; the three unpaired electrons are in the 6p orbitals.
93. Hg: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}$
- a. From the electron configuration for Hg, we have $3s^2$, $3p^6$, and $3d^{10}$ electrons; 18 total electrons with $n = 3$.
- b. $3d^{10}$, $4d^{10}$, $5d^{10}$; 30 electrons are in the d atomic orbitals.
- c. $2p^6$, $3p^6$, $4p^6$, $5p^6$; each set of np orbitals contain one p_z atomic orbital. Because we have 4 sets of np orbitals and two electrons can occupy the p_z orbital, there are $4(2) = 8$ electrons in p_z atomic orbitals.
- d. All the electrons are paired in Hg, so one-half of the electrons are spin up ($m_s = +1/2$) and the other half are spin down ($m_s = -1/2$). 40 electrons have spin up.
94. Element 115, Uup, is in Group 5A under Bi (bismuth):
- Uup: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^25f^{14}6d^{10}7p^3$
- a. $5s^2$, $5p^6$, $5d^{10}$, and $5f^{14}$; 32 electrons have $n = 5$ as one of their quantum numbers
- b. $\ell = 3$ are f orbitals. $4f^{14}$ and $5f^{14}$ are the f orbitals used. They are all filled, so 28 electrons have $\ell = 3$.
- c. p, d, and f orbitals all have one of the degenerate orbitals with $m_\ell = 1$. There are 6 orbitals with $m_\ell = 1$ for the various p orbitals used; there are 4 orbitals with $m_\ell = 1$ for the various d orbitals used; and there are 2 orbitals with $m_\ell = 1$ for the various f orbitals used. We have a total of $6 + 4 + 2 = 12$ orbitals with $m_\ell = 1$. Eleven of these orbitals are filled with

2 electrons, and the 7p orbitals are only half-filled. The number of electrons with $m_\ell = 1$ is $11 \times (2 e^-) + 1 \times (1 e^-) = 23$ electrons.

- d. The first 112 electrons are all paired; one-half of these electrons ($56 e^-$) will have $m_s = -1/2$. The 3 electrons in the 7p orbitals singly occupy each of the three degenerate 7p orbitals; the three electrons are spin parallel, so the 7p electrons either have $m_s = +1/2$ or $m_s = -1/2$. Therefore, either 56 electrons have $m_s = -1/2$ or 59 electrons have $m_s = -1/2$.

95. B: $1s^2 2s^2 2p^1$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	+1/2
1s	1	0	0	-1/2
2s	2	0	0	+1/2
2s	2	0	0	-1/2
2p*	2	1	-1	+1/2

*This is only one of several possibilities for the 2p electron. The 2p electron in B could have $m_\ell = -1, 0$ or $+1$ and $m_s = +1/2$ or $-1/2$ for a total of six possibilities.

N: $1s^2 2s^2 2p^3$

	n	ℓ	m_ℓ	m_s	
1s	1	0	0	+1/2	
1s	1	0	0	-1/2	
2s	2	0	0	+1/2	
2s	2	0	0	-1/2	
2p	2	1	-1	+1/2	}
2p	2	1	0	+1/2	
2p	2	1	+1	+1/2	

(Or all 2p electrons could have $m_s = -1/2$.)

96. Ti: $[\text{Ar}]4s^2 3d^2$

	n	ℓ	m_ℓ	m_s
4s	4	0	0	+1/2
4s	4	0	0	-1/2
3d	3	2	-2	+1/2
3d	3	2	-1	+1/2

Only one of 10 possible combinations of m_ℓ and m_s for the first d electron. For the ground state, the second d electron should be in a different orbital with spin parallel; 4 possibilities.

CHAPTER 2 ATOMIC STRUCTURE AND PERIODICITY

97. Group 1A: 1 valence electron; ns^1 ; Li: $[\text{He}]2s^1$; $2s^1$ is the valence electron configuration for Li.
 Group 2A: 2 valence electrons; ns^2 ; Ra: $[\text{Rn}]7s^2$; $7s^2$ is the valence electron configuration for Ra.
 Group 3A: 3 valence electrons; ns^2np^1 ; Ga: $[\text{Ar}]4s^23d^{10}4p^1$; $4s^24p^1$ is the valence electron configuration for Ga. Note that valence electrons for the representative elements of Groups 1A-8A are considered those electrons in the highest n value, which for Ga is $n = 4$. We do not include the 3d electrons as valence electrons because they are not in $n = 4$ level.
 Group 4A: 4 valence electrons; ns^2np^2 ; Si: $[\text{Ne}]3s^23p^2$; $3s^23p^2$ is the valence electron configuration for Si.
 Group 5A: 5 valence electrons; ns^2np^3 ; Sb: $[\text{Kr}]5s^24d^{10}5p^3$; $5s^25p^3$ is the valence electron configuration for Sb.
 Group 6A: 6 valence electrons; ns^2np^4 ; Po: $[\text{Xe}]6s^24f^{14}5d^{10}6p^4$; $6s^26p^4$ is the valence electron configuration for Po.
 Group 7A: 7 valence electrons; ns^2np^5 ; 117: $[\text{Rn}]7s^25f^{14}6d^{10}7p^5$; $7s^27p^5$ is the valence electron configuration for 117.
 Group 8A: 8 valence electrons; ns^2np^6 ; Ne: $[\text{He}]2s^22p^6$; $2s^22p^6$ is the valence electron configuration for Ne.
98. a. 2 valence electrons; $4s^2$ b. 6 valence electrons; $2s^22p^4$
 c. 7 valence electrons; $7s^27p^5$ d. 3 valence electrons; $5s^25p^1$
 e. 8 valence electrons; $3s^23p^6$ f. 5 valence electrons; $6s^26p^3$
99. O: $1s^22s^22p_x^22p_y^2$ ($\uparrow\downarrow \uparrow\downarrow _$); there are no unpaired electrons in this oxygen atom. This configuration would be an excited state, and in going to the more stable ground state ($\uparrow\downarrow \uparrow \uparrow$), energy would be released.
100. The number of unpaired electrons is in parentheses.
- | | | | |
|--------------------------------|-----|----------------------------------------|-----|
| a. excited state of boron | (1) | b. ground state of neon | (0) |
| B ground state: $1s^22s^22p^1$ | (1) | Ne ground state: $1s^22s^22p^6$ | (0) |
| c. excited state of fluorine | (3) | d. excited state of iron | (6) |
| F ground state: $1s^22s^22p^5$ | (1) | Fe ground state: $[\text{Ar}]4s^23d^6$ | (4) |
- $$\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow \\ 2p \end{array}$$

$$\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 3d \end{array}$$
101. None of the s block elements have 2 unpaired electrons. In the p block, the elements with either ns^2np^2 or ns^2np^4 valence electron configurations have 2 unpaired electrons. For elements 1-36, these are elements C, Si, and Ge (with ns^2np^2) and elements O, S, and Se (with ns^2np^4). For the d block, the elements with configurations nd^2 or nd^8 have two unpaired

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electrons. For elements 1-36, these are Ti ($3d^2$) and Ni ($3d^8$). A total of 8 elements from the first 36 elements have two unpaired electrons in the ground state.

102. The s block elements with ns^1 for a valence electron configuration have one unpaired electron. These are elements H, Li, Na, and K for the first 36 elements. The p block elements with ns^2np^1 or ns^2np^5 valence electron configurations have one unpaired electron. These are elements B, Al, and Ga (ns^2np^1) and elements F, Cl, and Br (ns^2np^5) for the first 36 elements. In the d block, Sc ($[Ar]4s^23d^1$) and Cu ($[Ar]4s^13d^{10}$) each have one unpaired electron. A total of 12 elements from the first 36 elements have one unpaired electron in the ground state.
103. We get the number of unpaired electrons by examining the incompletely filled subshells. The paramagnetic substances have unpaired electrons, and the ones with no unpaired electrons are not paramagnetic (they are called diamagnetic).

Li: $1s^2 2s^1 \uparrow$; paramagnetic with 1 unpaired electron.
 $\quad\quad\quad 2s$

N: $1s^2 2s^2 2p^3 \uparrow \uparrow \uparrow$; paramagnetic with 3 unpaired electrons.
 $\quad\quad\quad 2p$

Ni: $[Ar]4s^2 3d^8 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$; paramagnetic with 2 unpaired electrons.
 $\quad\quad\quad 3d$

Te: $[Kr]5s^2 4d^{10} 5p^4 \uparrow \downarrow \uparrow \uparrow$; paramagnetic with 2 unpaired electrons.
 $\quad\quad\quad 5p$

Ba: $[Xe]6s^2 \uparrow \downarrow$; not paramagnetic because no unpaired electrons are present.
 $\quad\quad\quad 6s$

Hg: $[Xe]6s^2 4f^{14} 5d^{10} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$; not paramagnetic because no unpaired electrons.
 $\quad\quad\quad 5d$

104. We get the number of unpaired electrons by examining the incompletely filled subshells.

O: $[He]2s^2 2p^4 \quad 2p^4: \uparrow \downarrow \uparrow \uparrow$ two unpaired e^-

O^+ : $[He]2s^2 2p^3 \quad 2p^3: \uparrow \uparrow \uparrow$ three unpaired e^-

O^- : $[He]2s^2 2p^5 \quad 2p^5: \uparrow \downarrow \uparrow \downarrow \uparrow$ one unpaired e^-

Os: $[Xe]6s^2 4f^{14} 5d^6 \quad 5d^6: \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$ four unpaired e^-

Zr: $[Kr]5s^2 4d^2 \quad 4d^2: \uparrow \uparrow _ _ _$ two unpaired e^-

S: $[Ne]3s^2 3p^4 \quad 3p^4: \uparrow \downarrow \uparrow \uparrow$ two unpaired e^-

F: $[He]2s^2 2p^5 \quad 2p^5: \uparrow \downarrow \uparrow \downarrow \uparrow$ one unpaired e^-

Ar: $[Ne]3s^2 3p^6 \quad 3p^6: \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ zero unpaired e^-

The Periodic Table and Periodic Properties

105. Size (radius) decreases left to right across the periodic table, and size increases from top to bottom of the periodic table.

- a. $S < Se < Te$ b. $Br < Ni < K$ c. $F < Si < Ba$

All follow the general radius trend.

106. a. $Be < Na < Rb$ b. $Ne < Se < Sr$ c. $O < P < Fe$

All follow the general radius trend.

107. The ionization energy trend is the opposite of the radius trend; ionization energy (IE), in general, increases left to right across the periodic table and decreases from top to bottom of the periodic table.

- a. $Te < Se < S$ b. $K < Ni < Br$ c. $Ba < Si < F$

All follow the general IE trend.

108. a. $Rb < Na < Be$ b. $Sr < Se < Ne$ c. $Fe < P < O$

All follow the general IE trend.

109. a. He (From the general radius trend.) b. Cl

c. Element 116 is the next oxygen family member to be discovered (under Po), element 119 is the next alkali metal to be discovered (under Fr), and element 120 is the next alkaline earth metal to be discovered (under Ra). From the general radius trend, element 116 will be the smallest.

d. Si

e. Na^+ ; this ion has the fewest electrons as compared to the other sodium species present. Na^+ has the smallest number of electron-electron repulsions, which makes it the smallest ion with the largest ionization energy.

110. a. Ba (From the general ionization energy trend.) b. K

c. O; in general, Group 6A elements have a lower ionization energy than neighboring Group 5A elements. This is an exception to the general ionization energy trend across the periodic table.

d. S^{2-} ; this ion has the most electrons compared to the other sulfur species present. S^{2-} has the largest number of electron-electron repulsions, which leads to S^{2-} having the largest size and smallest ionization energy.

e. Cs; this follows the general ionization energy trend.

111. a. Sg: $[\text{Rn}]7s^25f^{14}6d^4$ b. W, which is directly above Sg in the periodic table.
112. a. Uus will have 117 electrons. $[\text{Rn}]7s^25f^{14}6d^{10}7p^5$
 b. It will be in the halogen family and will be most similar to astatine (At).
113. As: $[\text{Ar}]4s^23d^{10}4p^3$; Se: $[\text{Ar}]4s^23d^{10}4p^4$; the general ionization energy trend predicts that Se should have a higher ionization energy than As. Se is an exception to the general ionization energy trend. There are extra electron-electron repulsions in Se because two electrons are in the same 4p orbital, resulting in a lower ionization energy for Se than predicted.
114. Expected order from IE trend: $\text{Be} < \text{B} < \text{C} < \text{N} < \text{O}$
 B and O are exceptions to the general IE trend. The IE of O is lower because of the extra electron-electron repulsions present when two electrons are paired in the same orbital. This makes it slightly easier to remove an electron from O compared to N. B is an exception because of the smaller penetrating ability of the 2p electron in B compared to the 2s electrons in Be. The smaller penetrating ability makes it slightly easier to remove an electron from B compared to Be. The correct IE ordering, taking into account the two exceptions, is $\text{B} < \text{Be} < \text{C} < \text{O} < \text{N}$.
115. a. As we remove succeeding electrons, the electron being removed is closer to the nucleus, and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus, and it takes more energy to remove these electrons.
 b. Al: $1s^22s^22p^63s^23p^1$; for I_4 , we begin removing an electron with $n = 2$. For I_3 , we remove an electron with $n = 3$ (the last valence electron). In going from $n = 3$ to $n = 2$, there is a big jump in ionization energy because the $n = 2$ electrons are closer to the nucleus on average than the $n = 3$ electrons. Since the $n = 2$ electrons are closer, on average, to the nucleus, they are held more tightly and require a much larger amount of energy to remove compared to the $n = 3$ electrons. In general, valence electrons are much easier to remove than inner-core electrons.
116. The general ionization energy trend says that ionization energy increases going left to right across the periodic table. However, one of the exceptions to this trend occurs between Groups 2A and 3A. Between these two groups, Group 3A elements usually have a lower ionization energy than Group 2A elements. Therefore, Al should have the lowest first ionization energy value, followed by Mg, with Si having the largest ionization energy. Looking at the values for the first ionization energy in the graph, the orange plot is Al, the blue plot is Mg, and the pink plot is Si.
 Mg (the blue plot) is the element with the huge jump between I_2 and I_3 . Mg has two valence electrons, so the third electron removed is an inner core electron. Inner core electrons are always much more difficult to remove than valence electrons since they are closer to the nucleus, on average, than the valence electrons.
117. a. More favorable EA: C and Br; the electron affinity trend is very erratic. Both N and Ar have positive EA values (unfavorable) due to their electron configurations (see text for detailed explanation).

- b. Higher IE: N and Ar (follows the IE trend)
- c. Larger size: C and Br (follows the radius trend)
118. a. More favorable EA: K and Cl; Mg has a positive EA value, and F has a more positive EA value than expected from its position relative to Cl.
- b. Higher IE: Mg and F c. Larger radius: K and Cl

ChemWork Problems

119. a. $\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{6.0 \times 10^{13} \text{ s}^{-1}} = 5.0 \times 10^{-6} \text{ m}$
- b. From Figure 2-2, this is infrared electromagnetic radiation.
- c. $E = h\nu = 6.63 \times 10^{-34} \text{ J s} \times 6.0 \times 10^{13} = 4.0 \times 10^{-20} \text{ J/photon}$
- d. Frequency and photon energy are directly related ($E = h\nu$). Because 5.4×10^{13} electromagnetic radiation (EMR) has a lower frequency than 6.0×10^{13} EMR, the 5.4×10^{13} EMR will have less energetic photons.

120. $60 \times 10^6 \text{ km} \times \frac{1000 \text{ m}}{\text{km}} \times \frac{1 \text{ s}}{3.00 \times 10^8 \text{ m}} = 200 \text{ s}$ (about 3 minutes)

121. a. $\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{3.59 \times 10^{-19} \text{ J}} = 5.53 \times 10^{-7} \text{ m} \times \frac{100 \text{ cm}}{\text{m}}$
 $= 5.53 \times 10^{-5} \text{ cm}$

From the spectrum, $\lambda = 5.53 \times 10^{-5} \text{ cm}$ is greenish-yellow light.

b. $\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{6^2} \right) = -4.840 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.840 \times 10^{-19} \text{ J}} = 4.104 \times 10^{-7} \text{ m} \times \frac{100 \text{ cm}}{\text{m}}$$

$$= 4.104 \times 10^{-5} \text{ cm}$$

From the spectrum, $\lambda = 4.104 \times 10^{-5} \text{ cm}$ is violet light, so the $n = 6$ to $n = 2$ visible spectrum line is violet.

122. The longest wavelength light emitted will correspond to the transition with the smallest energy change (smallest ΔE). This is the transition from $n = 5$ to $n = 4$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = -4.901 \times 10^{-20} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.901 \times 10^{-20} \text{ J}} = 4.053 \times 10^{-6} \text{ m} = 4053 \text{ nm}$$

The shortest wavelength emitted will correspond to the largest ΔE ; this is $n = 5 \rightarrow n = 1$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{5^2} \right) = -2.091 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.091 \times 10^{-18} \text{ J}} = 9.500 \times 10^{-8} \text{ m} = 95.00 \text{ nm}$$

123. There are 5 possible transitions for an electron in the $n = 6$ level ($6 \rightarrow 5$, $6 \rightarrow 4$, $6 \rightarrow 3$, $6 \rightarrow 2$, and $6 \rightarrow 1$). If an electron initially drops to the $n = 5$ level, four additional transitions can occur ($5 \rightarrow 4$, $5 \rightarrow 3$, $5 \rightarrow 2$, and $5 \rightarrow 1$). Similarly, there are three more transitions from the $n = 4$ level ($4 \rightarrow 3$, $4 \rightarrow 2$, $4 \rightarrow 1$), two more transitions from the $n = 3$ level ($3 \rightarrow 2$, $3 \rightarrow 1$), and one more transition from the $n = 2$ level ($2 \rightarrow 1$). There are a total of 15 possible transitions for an electron in the $n = 6$ level for a possible total of 15 different wavelength emissions.

124. Exceptions: Cr, Cu, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Pt, and Au; Tc, Ru, Rh, Pd, and Pt do not correspond to the supposed extra stability of half-filled and filled subshells.

125. a. True for H only. b. True for all atoms. c. True for all atoms.

126. $n = 5$; $m\ell = 4, 3, 2, 1, 0, 1, 2, 3, 4$; 18 electrons

127. $2f$ and $2d_{xy}$ orbitals are forbidden energy levels (they do not exist), so zero electrons can occupy these. The $3p$ and $4p$ sets each contain three degenerate orbitals, so each set can hold 6 electrons, and the $5d_{yz}$ represents a singular energy level which can hold 2 electrons.

128. As: $1s^2 2s^2 2p^6 3s^2 3p^4 4s^2 3d^1 4p^3$ $\ell = 1$ are p orbitals. $2p^6$, $3p^6$, and $4p^3$ are the p orbitals used. So 15 electrons have $\ell = 1$.

The s, p, and d orbitals all have one of the orbitals with $m\ell = 0$. There are four orbitals with $m\ell = 0$ from the various s orbitals used, there are three orbitals with $m\ell = 0$ from the various p orbitals used, and there is one orbital with $m\ell = 0$ from the 3d orbitals used. We have a total of $4 + 3 + 1 = 8$ orbitals with $m\ell = 0$. Seven of these orbitals are filled with 2 electrons, and the 4p orbitals are only half-filled. The number of electrons with $m\ell = 0$ is $7 \times (2 e^-) + 1 \times (1 e^-) = 15$ electrons.

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129. a. False, an electron in a 2s orbital would be on average, closer to the nucleus than an electron in a 3s orbital.
 b. True, the Bohr model is fundamentally incorrect
 c. True; d. False; these two terms come from different atomic structure models
 e. True; when $n = 3$, ℓ can equal 0 (s orbital), 1 (p orbitals), and 2 (d orbitals).

130. From the radii trend, the smallest-size element (excluding hydrogen) would be the one in the most upper right corner of the periodic table. This would be O. The largest-size element would be the one in the most lower left of the periodic table. Thus K would be the largest. The ionization energy (IE) trend is the exact opposite of the radii trend. So K, with the largest size, would have the smallest first ionization energy. From the general IE trend, O should have the largest ionization energy. However, there is an exception to the general IE trend between N and O. Due to this exception, N would have the largest first ionization energy of the elements examined.

131. a. This element has $36 + 2 + 10 + 4 = 52$ electrons. This is Te.
 b. This element has 32 electrons; this is Ge.
 c. This element has 9 electrons; so it is F.

132. All oxygen family elements have ns^2np^4 valence electron configurations, so this nonmetal is from the oxygen family.

- a. $2 + 4 = 6$ valence electrons.
 b. O, S, Se, and Te are the nonmetals from the oxygen family (Po is a metal).
 c. Potassium, like the other alkali metals, forms $1+$ charged ions when in compounds. Because oxygen family nonmetals form $2-$ charged ions in ionic compounds, K_2X would be the predicted formula, where X is the unknown nonmetal.
 d. From the size trend, this element would have a smaller radius than barium.
 e. From the ionization energy trend, this element would have a smaller ionization energy than fluorine.

133. a. True (follows general ionization energy trend)
 b. False; cations are smaller than the parent atom.
 c. False; all ionization energies are positive (energy must be added to remove electrons).
 d. True
 e. True; this is hard to predict because the general atomic radius trends go against each other when going from Li to Al. Figure 2-33 of the text was used to answer this question.

134.
$$\frac{476 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 7.90 \times 10^{-22} \text{ kJ} = 7.90 \times 10^{-19} \text{ J to remove one electron}$$

135.
$$E = \frac{310 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 5.15 \times 10^{-22} \text{ kJ} = 5.15 \times \quad \text{J/photon}$$

136. Applying the general trends in radii and ionization energy allows matching of the various values to the elements.

Mg : $1s^2 2s^2 2p^6 3s^2$: 0.734 MJ/mol : 160 pm

S : $1s^2 2s^2 2p^6 3s^2 3p^4$: 0.999 MJ/mol : 104 pm

Ca : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$: 0.590 MJ/mol : 197 pm

137. a. $[\text{Kr}]5s^2 4d^{10} 5p^6 = \text{Xe}$; $[\text{Kr}]5s^2 4d^{10} 5p^1 = \text{In}$; $[\text{Kr}]5s^2 4d^{10} 5p^3 = \text{Sb}$

From the general radii trend, the increasing size order is $\text{Xe} < \text{Sb} < \text{In}$.

b. $[\text{Ne}]3s^2 3p^5 = \text{Cl}$; $[\text{Ar}]4s^2 3d^{10} 4p^3 = \text{As}$; $[\text{Ar}]4s^2 3d^{10} 4p^5 = \text{Br}$

From the general IE trend, the decreasing IE order is $\text{Cl} > \text{Br} > \text{As}$.

138. a.
$$\nu = \frac{E}{h} = \frac{7.52 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.13 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.13 \times 10^{15} \text{ s}^{-1}} = 2.65 \times 10^{-7} \text{ m} = 265 \text{ nm}$$

b. E_{photon} and λ are inversely related ($E = hc/\lambda$). Any wavelength of electromagnetic radiation less than or equal to 265 nm ($\lambda \leq 265$) will have sufficient energy to eject an electron. So, yes, 259-nm electromagnetic radiation will eject an electron.

c. This is the electron configuration for copper, Cu, an exception to the expected filling order.

Challenge Problems

$$139. \quad E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{253.4 \times 10^{-9} \text{ m}} = 7.839 \times 10^{-19} \text{ J}$$

$\Delta E = 7.839 \times 10^{-19} \text{ J}$; the general energy equation for one-electron ions is $E_n = -2.178 \times 10^{-18} \text{ J} (Z^2/n^2)$, where $Z = \text{atomic number}$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} (Z)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad Z = 4 \text{ for Be}^{3+}$$

$$\Delta E = -7.839 \times 10^{-19} \text{ J} = -2.178 \times 10^{-18} (4)^2 \left(\frac{1}{n_f^2} - \frac{1}{5^2} \right)$$

$$\frac{7.839 \times 10^{-19}}{2.178 \times 10^{-18} \times 16} + \frac{1}{25} = \frac{1}{n_f^2}, \quad \frac{1}{n_f^2} = 0.06249, \quad n_f = 4$$

This emission line corresponds to the $n = 5 \rightarrow n = 4$ electronic transition.

140. a. Because wavelength is inversely proportional to energy, the spectral line to the right of (at a larger wavelength) represents the lowest possible energy transition; this is $n = 4$ to $n = 3$. The B line represents the next lowest energy transition, which is $n = 5$ to $n = 3$, and the A line corresponds to the $n = 6$ to $n = 3$ electronic transition.
- b. Because this spectrum is for a one-electron ion, $E_n = -2.178 \times 10^{-18} \text{ J} (Z^2/n^2)$. To determine ΔE and, in turn, the wavelength of spectral line A, we must determine Z , the atomic number of the one electron species. Use spectral line B data to determine Z .

$$\Delta E_{5 \rightarrow 3} = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{3^2} - \frac{Z^2}{5^2} \right) = -2.178 \times 10^{-18} \left(\frac{16Z^2}{9 \times 25} \right)$$

$$E = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} (2.9979 \times 10^8 \text{ m/s})}{142.5 \times 10^{-9} \text{ m}} = 1.394 \times 10^{-18} \text{ J}$$

Because an emission occurs, $\Delta E_{5 \rightarrow 3} = -1.394 \times 10^{-18} \text{ J}$.

$$\Delta E = -1.394 \times 10^{-18} \text{ J} = -2.178 \times 10^{-18} \text{ J} \left(\frac{16Z^2}{9 \times 25} \right), \quad Z^2 = 9.001, \quad Z = 3; \text{ the ion is Li}^{2+}.$$

Solving for the wavelength of line A:

$$\Delta E_{6 \rightarrow 3} = -2.178 \times 10^{-18} (3)^2 \left(\frac{1}{3^2} - \frac{1}{6^2} \right) = -1.634 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} (2.9979 \times 10^8 \text{ m/s})}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm}$$

141. For hydrogen: $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = -4.574 \times 10^{-19} \text{ J}$

For a similar blue light emission, He^+ will need about the same ΔE value.

For He^+ : $E_n = -2.178 \times 10^{-18} \text{ J} (Z^2/n^2)$, where $Z = 2$:

$$\Delta E = -4.574 \times 10^{-19} \text{ J} = -2.178 \times 10^{-18} \text{ J} \left(\frac{2^2}{n_f^2} - \frac{2^2}{4^2} \right)$$

$$0.2100 = \frac{4}{n_f^2} - \frac{4}{16}, \quad 0.4600 = \frac{4}{n_f^2}, \quad n_f = 2.949$$

The transition from $n = 4$ to $n = 3$ for He^+ should emit a similar colored blue light as the $n = 5$ to $n = 2$ hydrogen transition; both these transitions correspond to very nearly the same energy change.

142. For one-electron species, $E_n = -R_H Z^2/n^2$. IE is for the $n = 1 \rightarrow n = \infty$ transition. So:

$$\text{IE} = E_\infty - E_1 = -E_1 = R_H Z^2/n^2 = R_H Z^2$$

$$4.72 \times 10^4 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 2.178 \times 10^{-18} \text{ J} (Z^2); \text{ solving: } Z = 6$$

Element 6 is carbon ($X = \text{carbon}$), and the charge for a one-electron carbon ion is $5+$ ($m = 5$). The one-electron ion is C^{5+} .

143. A node occurs when $\psi = 0$. $\psi_{300} = 0$ when $27 - 18\sigma + 2\sigma^2 = 0$.

$$\text{Solving using the quadratic formula: } \sigma = \frac{18 \pm \sqrt{(18)^2 - 4(2)(27)}}{4} = \frac{18 \pm \sqrt{108}}{4}$$

$\sigma = 7.10$ or $\sigma = 1.90$; because $\sigma = r/a_0$, the nodes occur at $r = (7.10)a_0 = 3.76 \times 10^{-10} \text{ m}$ and at $r = (1.90)a_0 = 1.01 \times 10^{-10} \text{ m}$, where r is the distance from the nucleus.

144. For $r = a_0$ and $\theta = 0^\circ$ ($Z = 1$ for H):

$$\psi_{2p_z} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{5.29 \times 10^{-11}} \right)^{3/2} (1) e^{-1/2} \cos 0 = 1.57 \times 10^{14}; \quad \psi^2 = 2.46 \times 10^{28}$$

For $r = a_0$ and $\theta = 90^\circ$, $\psi_{2p_z} = 0$ since $\cos 90^\circ = 0$; $\psi^2 = 0$; there is no probability of finding an electron in the $2p_z$ orbital with $\theta = 90^\circ$. As expected, the xy plane, which corresponds to $\theta = 90^\circ$, is a node for the $2p_z$ atomic orbital.

145. a. Each orbital could hold 3 electrons.

b. The first period corresponds to $n = 1$ which can only have 1s orbitals. The 1s orbital could hold 3 electrons; hence the first period would have three elements. The second

CHAPTER 2 ATOMIC STRUCTURE AND PERIODICITY

period corresponds to $n = 2$, which has 2s and 2p orbitals. These four orbitals can each hold three electrons. A total of 12 elements would be in the second period.

- c. 15 d. 21

146. a. 1st period: $p = 1, q = 1, r = 0, s = \pm 1/2$ (2 elements)
2nd period: $p = 2, q = 1, r = 0, s = \pm 1/2$ (2 elements)
3rd period: $p = 3, q = 1, r = 0, s = \pm 1/2$ (2 elements)
 $p = 3, q = 3, r = -2, s = \pm 1/2$ (2 elements)
 $p = 3, q = 3, r = 0, s = \pm 1/2$ (2 elements)
 $p = 3, q = 3, r = +2, s = \pm 1/2$ (2 elements)
4th period: $p = 4$; q and r values are the same as with $p = 3$ (8 total elements)

1							2
3							4
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

- b. Elements 2, 4, 12, and 20 all have filled shells and will be least reactive.
c. Draw similarities to the modern periodic table.

XY could be X^+Y^- , $X^{2+}Y^{2-}$, or $X^{3+}Y^{3-}$. Possible ions for each are:

X^+ could be elements 1, 3, 5, or 13; Y^- could be 11 or 19.

X^{2+} could be 6 or 14; Y^{2-} could be 10 or 18.

X^{3+} could be 7 or 15; Y^{3-} could be 9 or 17.

Note: X^{4+} and Y^{4-} ions probably won't form.

XY_2 will be $X^{2+}(Y^-)_2$; See above for possible ions.

X_2Y will be $(X^+)_2Y^{2-}$ See above for possible ions.

XY_3 will be $X^{3+}(Y^-)_3$; See above for possible ions.

X_2Y_3 will be $(X^{3+})_2(Y^{2-})_3$; See above for possible ions.

d. $p = 4, q = 3, r = -2, s = \pm 1/2$ (2 electrons)

$p = 4, q = 3, r = 0, s = \pm 1/2$ (2 electrons)

$p = 4, q = 3, r = +2, s = \pm 1/2$ (2 electrons)

A total of 6 electrons can have $p = 4$ and $q = 3$.

e. $p = 3, q = 0, r = 0$; this is not allowed; q must be odd. Zero electrons can have these quantum numbers.

f. $p = 6, q = 1, r = 0, s = \pm 1/2$ (2 electrons)

$p = 6, q = 3, r = -2, 0, +2; s = \pm 1/2$ (6 electrons)

$p = 6, q = 5, r = -4, -2, 0, +2, +4; s = \pm 1/2$ (10 electrons)

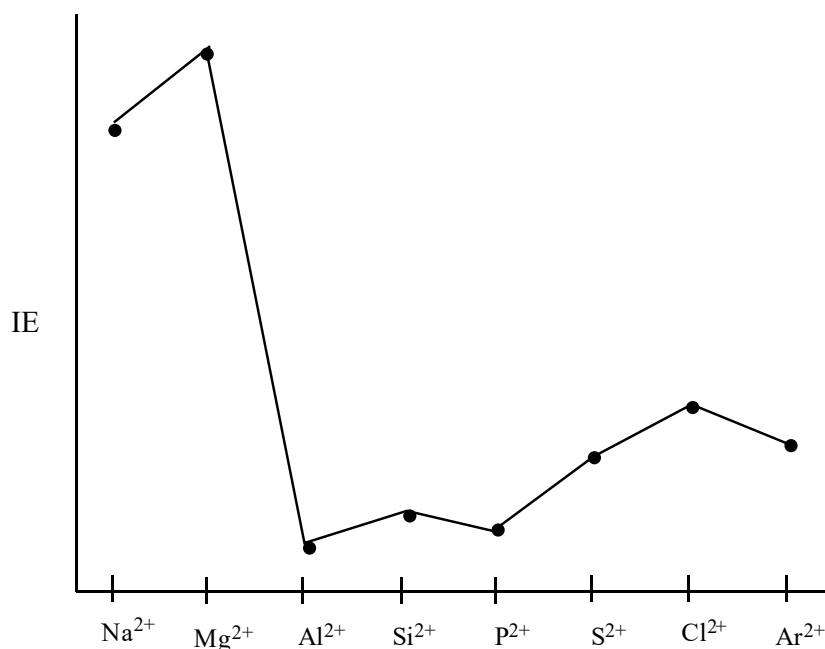
Eighteen electrons can have $p = 6$.

147. IE_3 refers to: $E^{2+}(g) \rightarrow E^{3+}(g) + e^-$. The electron configurations for the 2+ charged ions of Na to Ar are:

Na^{2+} :	$1s^2 2s^2 2p^5$	Al^{2+} : $[Ne]3s^1$
Mg^{2+} :	$1s^2 2s^2 2p^6$	Si^{2+} : $[Ne]3s^2$
		P^{2+} : $[Ne]3s^2 3p^1$
		S^{2+} : $[Ne]3s^2 3p^2$
		Cl^{2+} : $[Ne]3s^2 3p^3$
		Ar^{2+} : $[Ne]3s^2 3p^4$

IE_3 for sodium and magnesium should be extremely large compared with the others because $n = 2$ electrons are much more difficult to remove than $n = 3$ electrons. Between Na^{2+} and Mg^{2+} , one would expect to have the same trend as seen with $IE_1(F)$ versus $IE_1(Ne)$; these neutral atoms have identical electron configurations to Na^{2+} and Mg^{2+} . Therefore, the $1s^2 2s^2 2p^5$ ion (Na^{2+}) should have a lower ionization energy than the $1s^2 2s^2 2p^6$ ion (Mg^{2+}).

The remaining 2+ ions (Al^{2+} to Ar^{2+}) should follow the same trend as the neutral atoms having the same electron configurations. The general IE trend predicts an increase from $[Ne]3s^1$ to $[Ne]3s^2 3p^4$. The exceptions occur between $[Ne]3s^2$ and $[Ne]3s^2 3p^1$ and between $[Ne]3s^2 3p^3$ and $[Ne]3s^2 3p^4$. $[Ne]3s^2 3p^1$ is out of order because of the small penetrating ability of the 3p electron as compared with the 3s electrons. $[Ne]3s^2 3p^4$ is out of order because of the extra electron-electron repulsions present when two electrons are paired in the same orbital. Therefore, the correct ordering for Al^{2+} to Ar^{2+} should be $Al^{2+} < P^{2+} < Si^{2+} < S^{2+} < Ar^{2+} < Cl^{2+}$, where P^{2+} and Ar^{2+} are out of line for the same reasons that Al and S are out of line in the general ionization energy trend for neutral atoms.



Note: The actual numbers in Table 2-5 support most of this plot. No IE_3 is given for Na^{2+} , so you cannot check this. The only deviation from our discussion is IE_3 for Ar^{2+} which is greater than IE_3 for Cl^{2+} instead of less than.

148. a. Assuming the Bohr model applies to the 1s electron, $E_{1s} = -RHZ^2/n^2 = -RHZ_{eff}^2$, where

$$n = 1. \text{ Ionization energy} = E_{\infty} - E_{1s} = 0 - E_{1s} = RHZ_{eff}^2.$$

$$\frac{2.462 \times 10^6 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 2.178 \times 10^{-18} \text{ J } (Z_{eff})^2, \quad Z_{eff} = 43.33$$

- b. Silver is element 47, so $Z = 47$ for silver. Our calculated Z_{eff} value is less than 47. Electrons in other orbitals can penetrate the 1s orbital. Thus a 1s electron can be slightly shielded from the nucleus by these penetrating electrons, giving a Z_{eff} close to but less than Z .

149. The ratios for Mg, Si, P, Cl, and Ar are about the same. However, the ratios for Na, Al, and S are higher. For Na, the second IE is extremely high because the electron is taken from $n = 2$ (the first electron is taken from $n = 3$). For Al, the first electron requires a bit less energy than expected by the trend due to the fact it is a 3p electron versus a 3s electron. For S, the first electron requires a bit less energy than expected by the trend due to electrons being paired in one of the p orbitals.

150. Size also decreases going across a period. Sc and Ti along with Y and Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.