CHAPTER 9

THE PERIODIC TABLE AND SOME ATOMIC PROPERTIES

PRACTICE EXAMPLES

1A Atomic size decreases from left to right across a period, and from bottom to top in a family. We expect the smallest elements to be in the upper right corner of the periodic table. S is the element closest to the upper right corner and thus should have the smallest atom.
$S = 104 \text{ pm} \quad As = 121 \text{ pm} \quad I = 133 \text{ pm}$

1B From the periodic table inside the front cover, we see that Na is in the same period as Al (period 3), but in a different group from K, Ca, and Br (period 4), which might suggest that Na and Al are about the same size. However, there is a substantial decrease in size as one moves from left to right in a period due to an increase in effective nuclear charge. Enough in fact, that Ca should be about the same size as Na.

2A Ti^{2+} and V^{3+} are isoelectronic; the one with higher positive charge should be smaller: $V^{3+} < Ti^{2+}$. Sr^{2+} and Br^- are isoelectronic; again, the one with higher positive charge should be smaller: $Sr^{2+} < Br^-$. In addition Ca^{2+} and Sr^{2+} both are ions of Group 2A; the one of lower atomic number should be smaller. $Ca^{2+} < Sr^{2+} < Br^-$. Finally, we know that the size of atoms decreases from left to right across a period; we expect sizes of like-charged ions to follow the same trend: $Ti^{2+} < Ca^{2+}$. The species are arranged below in order of increasing size.

$$V^{3+}(64 \text{ pm}) < Ti^{2+}(86 \text{ pm}) < Ca^{2+}(100 \text{ pm}) < Sr^{2+}(113 \text{ pm}) < Br^-(196 \text{ pm})$$

2B Br^- clearly is larger than As since Br^- is an anion in the same period as As. In turn, As is larger than N since both are in the same group, with As lower down in the group.
As also should be larger than P, which is larger than Mg^{2+}, an ion smaller than N. All that remains is to note that Cs is a truly large atom, one of the largest in the periodic table.
The As atom should be in the middle. Data from Figure 9-8 shows:
$65 \text{ pm for } Mg^{2+} < 70 \text{ pm for N} < 125 \text{ pm for As} < 196 \text{ pm for } Br^- < 265 \text{ pm for Cs}$

3A Ionization increases from bottom to top of a group and from left to right through a period. The first ionization energy of K is less than that of Mg and the first ionization energy of S is less than that of Cl. We would expect also that the first ionization energy of Mg is smaller than that of S, because Mg is a metal.

3B We would expect an alkali metal (Rb) or an alkaline earth metal (Sr) to have a low first ionization energy and nonmetals (e.g., Br) to have relatively high first ionization energies. Metalloids (such as Sb and As) should have intermediate ionization energies. Since the first ionization energy for As is larger than that for Sb, the first ionization energy of Sb should be in the middle.

4A Cl and Al must be paramagnetic, since each has an odd number of electrons. The electron configurations of K^+ ([Ar]) and O^{2-} ([Ne]) are those of the nearest noble gas. Because all of the electrons are paired, they are diamagnetic species. In Zn: [Ar] $3d^{10}4s^2$ all electrons are paired and so the atom is diamagnetic.

4B The electron configuration of Cr is [Ar] $3d^5 4s^1$; it has six unpaired electrons. The electron configuration of Cr^{2+} is [Ar] $3d^4$; it has four unpaired electrons. The electron configuration of Cr^{3+} is [Ar] $3d^3$; it has three unpaired electrons. Thus, of the two ions, Cr^{2+} has the greater number of unpaired electrons.

5A We expect the melting point of bromine to be close to the average of those for chlorine and iodine. Thus, the estimated melting point of $Br_2 = \dfrac{172\text{ K} + 387\text{ K}}{2} = 280\text{ K}$. The actual melting point is 266 K.

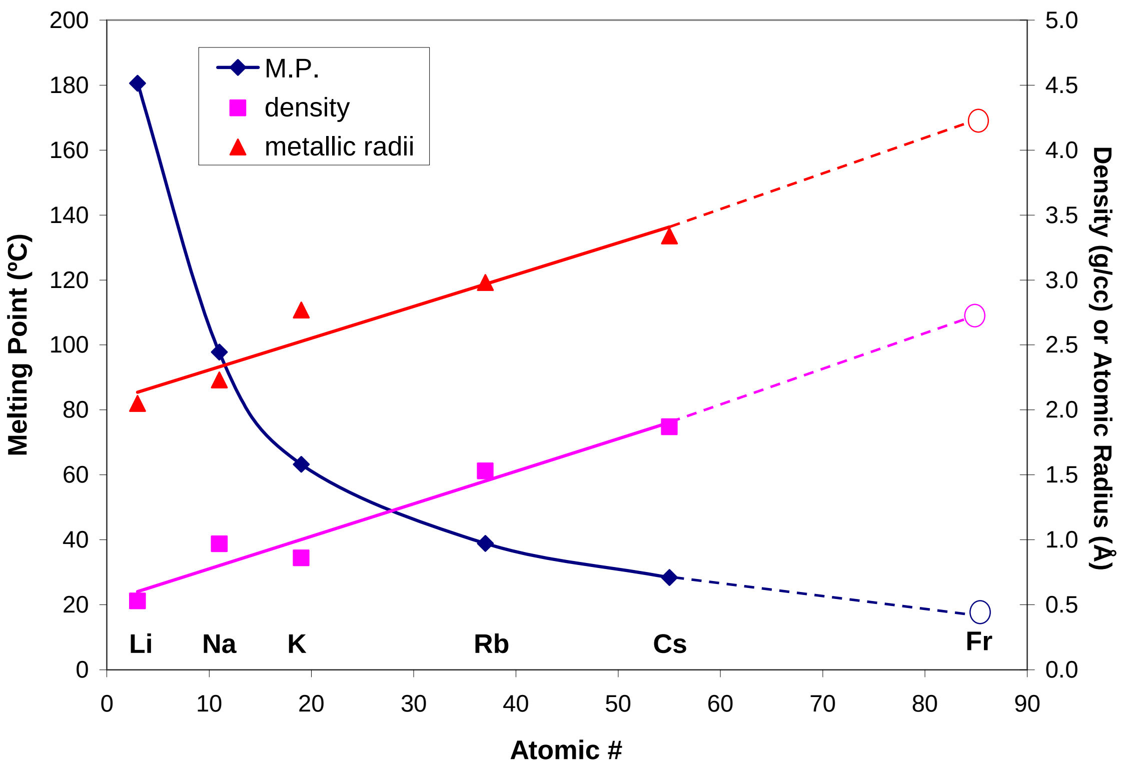
5B If the boiling point of I_2 (458 K) is the average of the boiling points of Br_2 (349 K) and At_2, then $458\text{ K} = \left(349\text{ K} + ?\right)/2 \qquad ? = 2 \times 458\text{ K} - 349\text{ K} = 567\text{ K}$

The estimated boiling point of molecular astatine is about 570 K.

INTEGRATIVE EXAMPLE

A. The physical properties of elements in the same period follow general trends. Below is a tabulation of the melting points, densities, and atomic radii of the alkali earth metals.

	Z	M.P. (ºC)	Density (g/cc)	Metallic Radii (Å)
Li	3	180.54	0.53	2.05
Na	11	97.81	0.97	2.23
K	19	63.25	0.86	2.77
Rb	37	38.89	1.53	2.98
Cs	55	28.4	1.87	3.34



Accompanying this table is the plot of the data. Based on rough approximations of the trends of data, the properties of francium can be approximated as follows:

Melting point: 22 °C, density: 2.75 g/cc, atomic radius: 4.25 Å

B. Element 168 should be a solid since the trend in boiling point and melting point would put the boililng point temperature above 298 K. The electronic configuration is [Unk]$10s^2 6h^8$.

EXERCISES

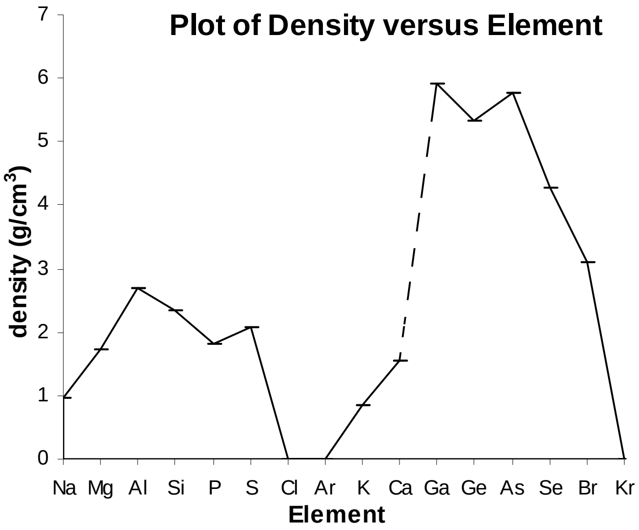
The Periodic Law

1. Element 114 will be a metal in the same group as Pb, element 82 (18 cm^3/mol); Sn, element 50 (18 cm^3/mol); and Ge, element 32 (14 cm^3/mol). We note that the atomic volumes of Pb and Sn are essentially equal, probably due to the lanthanide contraction. If there is also an actinide contraction, element 114 will have an atomic volume of 18 cm^3/mol. If there is no actinide contraction, we would predict a molar volume of ~ 22 cm^3 / mol. This need to estimate atomic volume is what makes the value for density questionable.

$$\text{density}\left(\frac{\text{g}}{\text{cm}^3}\right)=\frac{298\ \frac{\text{g}}{\text{mol}}}{18\ \frac{\text{cm}^3}{\text{mol}}}=16\ \frac{\text{g}}{\text{cm}^3}\qquad \text{density}\left(\frac{\text{g}}{\text{cm}^3}\right)=\frac{298\ \frac{\text{g}}{\text{mol}}}{22\ \frac{\text{cm}^3}{\text{mol}}}=14\ \frac{\text{g}}{\text{cm}^3}$$

3. The following data are plotted at right. Density clearly is a periodic property for these two periods of main group elements. It rises, falls a bit, rises again, and falls back to the axis, in both cases.

Element	Atomic Number Z	Density g/cm^3
Na	11	0.968
Mg	12	1.738
Al	13	2.699
Si	14	2.336
P	15	1.823
S	16	2.069
Cl	17	0.0032
Ar	18	0.0018
K	19	0.856
Ca	20	1.550
Ga	31	5.904
Ge	32	5.323
As	33	5.778
Se	34	4.285
Br	35	3.100
Kr	36	0.0037



The Periodic Table

5. Mendeleev arranged elements in the periodic table in order of increasing atomic weight. Of course, atomic masses with non-integral values are permissible. Hence, there always is room for an added element between two elements that already are present in the table. On the other hand, Moseley arranged elements in order of increasing atomic number. Only integral (whole number) values of atomic number are permitted. Thus, when elements with all possible integral values in a certain range have been discovered, no new elements are possible in that range.

7. **(a)** The noble gas following radon $(Z=86)$ will have an atomic number of $(86+32=)\,118$.

(b) The alkali metal following francium $(Z=87)$ will have an atomic number of $(87+32=)\,119$.

(c) The mass number of radon $(A=222)$ is $(222 \div 86 =)\,2.58$ times its atomic number.

The mass number of Lr $(A=262)$ is $(262 \div 103 =)\,2.54$ times its atomic number.

Thus, we would expect the mass numbers, and hence approximate atomic masses, of elements 118 and 119 to be about 2.5 times their atomic numbers, that is, $A_{119} \approx 298$ u and $A_{118} \approx 295$ u.

Atomic Radii and Ionic Radii

9. In general, atomic size in the periodic table increases from top to bottom for a group and increases from right to left through a period, as indicated in Figures 9-4 and 9-8. The larger element is indicated first, followed by the reason for making the choice.

(a) Te: Te is to the left of Br and also in the period below that of Br in the 4th period.
(b) K: K is to the left of Ca within the same period, Period 4.
(c) Cs : Cs is both below and to the left of Ca in the periodic table.
(d) N: N is to the left of O within the same period, Period 2.
(e) P: P is both below and to the left of O in the periodic table.
(f) Au: Au is both below and to the left of Al in the periodic table.

11. Sizes of atoms do not simply increase with atomic number is because electrons often are added successively to the same subshell. These electrons do not fully screen each other from the nuclear charge (they do not effectively get between each other and the nucleus). Consequently, as each electron is added to a subshell and the nuclear charge increases by one unit, all of the electrons in this subshell are drawn more closely into the nucleus, because of the ineffective shielding.

13. **(a)** The smallest atom in Group 13 is the first: B

(b) Po is in the sixth period, and is larger than the others, which are rewritten in the following list from left to right in the fifth period, that is, from largest to smallest: Sr, In, Sb, Te. Thus, Te is the smallest of the elements given.

15. Li^+ is the smallest; it not only is in the second period, but also is a cation. I^- is the largest, an anion in the fifth period. Next largest is Se in the previous (the fourth) period. We expect Br to be smaller than Se because it is both to the right of Se and in the same period.

$$\text{Li}^+ < \text{Br} < \text{Se} < \text{I}^-$$

17. In the literal sense, isoelectronic means having the same number and types of electrons. (In another sense, not used in the text, it means having the same electron configuration.) We determine the total number of electrons and the electron configuration for each species and make our decisions based on this information.

Fe^{2+}	24 electrons	$[\text{Ar}]\ 3d^6$	Sc^{3+}	18 electrons	$[\text{Ar}]$
Ca^{2+}	18 electrons	$[\text{Ar}]$	F^-	10 electrons	$[\text{He}]\ 2s^2 2p^6$
Co^{2+}	25 electrons	$[\text{Ar}]\ 3d^7$	Co^{3+}	24 electrons	$[\text{Ar}]\ 3d^6$
Sr^{2+}	36 electrons	$[\text{Ar}]\ 3d^{10} 4s^2 4p^6$	Cu^+	28 electrons	$[\text{Ar}]\ 3d^{10}$
Zn^{2+}	28 electrons	$[\text{Ar}]\ 3d^{10}$	Al^{3+}	10 electrons	$[\text{He}]\ 2s^2 2p^6$

Thus the species with the same number of electrons and the same electron configuration are the following. Fe^{2+} and Co^{3+} Sc^{3+} and Ca^{2+} F^- and Al^{3+} Zn^{2+} and Cu^+

19. Ions can be isoelectronic without having noble-gas electron configurations. Take, for instance, Cu^+ and Zn^{2+}. Both of these ions have the electron configuration $[\text{Ar}]3d^{10}$.

Ionization Energies; Electron Affinities

21. Ionization energy in the periodic table decreases from top to bottom for a group, and increases from left to right for a period, as summarized in Figure 9-10. Cs has the lowest ionization energy as it is farthest to the left and nearest to the bottom of the periodic table. Next comes Sr, followed by As, then S, and finally F, the most nonmetallic element in the group (and in the periodic table). Thus, the elements listed in order of increasing ionization energy are:

$$\text{Cs} < \text{Sr} < \text{As} < \text{S} < \text{F}$$

23. In the case of a first electron affinity, a negative electron is being added to a neutral atom. This process may be either exothermic or endothermic depending upon the electronic configuration of the atom. Energy tends to be released when filled shells or filled subshells are generated. In the case of an ionization potential, however, a negatively charged electron is being separated from a positively charged cation, a process that must always require energy, because unlike charges attract each other.

25. Ionization energies for Si: $I_1 = 786.5$ kJ/mol, $I_2 = 1577$ kJ/mol, $I_3 = 3232$ kJ/mol, $I_4 = 4356$ kJ/mol. To remove all four electrons from the third shell ($3s^23p^2$) would require the sum of all four ionization energies or $9951.\underline{5}$ kJ/mol. This would be 9.952×10^6 J per mole of Si atoms.

27. The electron affinity of bromine is -324.6 kJ/mol (Figure 9-10). We use Hess's law to determine the heat of reaction for $\text{Br}_2(\text{g})$ becoming $2\ \text{Br}^-(\text{g})$.

$$\text{Br}_2(\text{g}) \rightarrow 2\,\text{Br(g)} \qquad \Delta H = +193\ \text{kJ}$$

$$2\ \text{Br}(\text{g}) + 2\ \text{e}^- \rightarrow 2\ \text{Br}^-(\text{g}) \qquad 2\times E.A. = 2(-324.6)\ \text{kJ}$$

$$\text{Br}_2(\text{g}) + 2\ \text{e}^- \rightarrow 2\ \text{Br}^-(\text{g}) \qquad \Delta H = -456\ \text{kJ}$$

Overall process is *exothermic*.

29. The electron is being removed from a species with a neon electron configuration. But in the case of Na^+, the electron is being removed from a species that is left with a 2+ charge, while in the case of Ne, the electron is being removed from a species with a 1+ charge. The more highly charged the resulting species, the more difficult it is to produce it by removing an electron.

31. **(a)** Ionization energy in the periodic table decreases from top to bottom in a group, and increases from left to right across a period, as summarized in Figure 9-10. Therefore, the elements listed in order of increasing ionization energy are:

$$\text{Al} < \text{Si} < \text{S} < \text{Cl}$$

(b) Electron affinity is the measure of the energy change that occurs when a gaseous atom gains an electron. If energy is given off when this occurs, the process is exothermic and the electron affinity is negative. It is harder to make generalizations about electron affinities. If an atom has a high affinity for an electron, the electon affinity tends to be a large negative value. Chlorine hast the greatest affinity for an electron, becuase it will have a noble gas configuration when this occurs. In this series, aluminum has the smallest affinity for an electron. Therefore, the elements listed in order of increasing electron affinity are:

$$\text{Al} < \text{Si} < \text{S} < \text{Cl}$$

Magnetic Properties

33. Three of the ions have noble gas electron configurations and thus have no unpaired electrons: F^- is $1s^2 2s^2 2p^6$ Ca^{2+} and S^{2-} are $[Ne]3s^2 3p^6$

Only Fe^{2+} has unpaired electrons. Its electron configuration is $[Ar]\,3d^6$.

35. **(a)** K^+ is isoelectronic with Ar, with no unpaired electrons. It is diamagnetic.
(b) Cr^{3+} has the configuration $[Ar]3d^3$ with three unpaired electrons. It is paramagnetic.
(c) Zn^{2+} has the configuration $[Ar]3d^{10}$, with no unpaired electrons. It is diamagnetic.
(d) Cd has the configuration $[Kr]4d^{10}5s^2$, with no unpaired electrons. It is diamagnetic.
(e) Co^{3+} has the configuration $[Ar]3d^6$ with four unpaired electrons. It is paramagnetic
(f) Sn^{2+} has the configuration $[Kr]4d^{10}5s^2$, with no unpaired electrons. It is diamagnetic.
(g) Br has the configuration $[Ar]3d^{10}4s^2 5p^5$ with one unpaired electron. It is paramagnetic.
From this, we see that (a), (c), (d), and (f) are diamagnetic and (b), (e), and (g) are paramagnetic.

37. All atoms with an odd number of electrons must be paramagnetic. There is no way to pair all of the electrons up if there is an odd number of electrons. Many atoms with an even number of electrons are diamagnetic, but some are paramagnetic. The one of lowest atomic number is carbon $(Z = 6)$, which has two unpaired *p*-electrons producing the paramagnetic behavior: $[He]\ 2s^2 2p^2$.

Predictions Based on the Periodic Table

39. **(a)** Elements that one would expect to exhibit the photoelectric effect with visible light should be ones that have a small value of their first ionization energy. Based on Figure 9-9, the alkali metals have the lowest first ionization potentials of these. Cs, Rb, and K are three suitable metals. Metals that would not exhibit the photoelectric effect with visible light are those that have high values of their first ionization energy. Again from Figure 9-9, Zn, Cd, and Hg seem to be three metals that would not exhibit the photoelectric effect with visible light.

(b) From Figure 9-1, we notice that the atomic (molar) volume increases for the solid forms of the noble gases as we travel down the group (the data points just before the alkali metal peaks). But it seems to increase less rapidly than the molar mass. This means that the density should increase with atomic mass, and Rn should be the densest solid in the group. We expect densities of liquids to follow the same trend as densities of solids.

(c) To estimate the first ionization energy of fermium, we note in Figure 9-9 that the ionization energies of the lanthanides (following the Cs valley) are approximately the same. We expect similar behavior of the actinides, and estimate a first ionization energy of about +600 kJ/mol.

(d) We can estimate densities of solids from the information in Figure 9-1. Radium has $Z = 88$ and an approximate atomic volume of 40 cm^3/mol. Then we use the molar mass of radium to determine its density:

$$\text{density} = \frac{1\text{ mol}}{40\text{ cm}^3} \times \frac{226\text{ g Ra}}{1\text{ mol}} = 5.7\text{ g}/\text{cm}^3$$

41. **(a)**From Figure 9-1, the atomic (molar) volume of Al is 10 cm^3/mol and that for In is 15 cm^3/mol. Thus, we predict 12.5 cm^3/mol as the molar volume for Ga. Then we compute the expected density for Ga.

$$\text{density} = \frac{1\text{ mol Ga}}{12.5\text{ cm}^3} \times \frac{68\text{ g Ga}}{1\text{ mol Ga}} = 5.4\text{ g/cm}^3$$

(b) Since Ga is in group 13 (3A) (Gruppe III on Mendeleev's table), the formula of its oxide should be Ga_2O_3. We use Mendeleev's molar masses to determine the molar mass for Ga_2O_3. Molar mass $= 2\times 68\text{ g Ga} + 3\times 16\text{ g O} = 184\text{ g Ga}_2\text{O}_3$

$$\%\text{ Ga} = \frac{2\times 68\text{ g Ga}}{184\text{ g Ga}_2\text{O}_3} \times 100\% = 74\%(\text{Ga});$$

Using our more recent periodic table, we obtain 74.5% Ga.

43. We expect periodic properties to be functions of atomic number.

Element, atomic number	He, 2	Ne, 10	Ar, 18	Kr, 36	Xe, 54	Rn, 86
Boiling point, K	4.2 K	27.1 K	87.3 K	119.7 K	165 K	
Δ b.p. / Δ Z		2.86	7.5	1.8	2.5	

With one notable exception, we see that the boiling point increases about 2.4 K per unit of atomic number. The atomic number increases by 32 units from Xe to Rn. We might expect the boiling point to increase by $(2.4\times 32 =)\ 77$ K to $(165 + 77 =)\ 242$ K for Rn.

A simpler manner is to expect that the boiling point of xenon (165 K) is the average of the boiling points of radon and krypton (120 K).

$165\text{ K} = (120\text{ K} + ?)/2 \quad ? = 2\times 165\text{ K} - 120\text{ K} = 210\text{ K} =$ boiling point of radon

Often the simplest way is best. The tabulated value is 211 K.

(b) The boiling point decreases by 39 °C from H_2Te to H_2Se, and by 20 °C from H_2Se to H_2S. It probably will decrease by about 10 °C to reach H_2O. Therefore, one predicts a value for the boiling point of H_2O of approximately -71 °C. Of course, the actual boiling point of water is 100° C. The prediction is seriously in error (~ 170 °C) because we have neglected the hydrogen bonding between water molecules, a topic that is discussed in Chapter 13.

F	[He] $2s^2 2p^5$	1 unpaired e^-	N [He] $2s^2 2p^3$	3 unpaired e^-
S^{2-}	[Ne] $3s^2 3p^6$	0 unpaired e^-	Mg^{2+} [He] $2s^2 2p^6$	0 unpaired e^-
Sc^{3+}	[Ne] $3s^2 3p^6$	0 unpaired e^-	Ti^{3+} [Ar] $3d^1$	1 unpaired e^-

45.

(a) $Z = 32$ 1. This is the element Ge, with an outer electron configuration of $3s^2 3p^2$. Thus, Ge has two unpaired p electrons.

(b) $Z = 8$ 1. This is the element O. Each atom has an outer electron configuration of $2s^2 2p^4$. Thus, O has two unpaired p electrons.

(c) $Z = 53$ 3. This is the element I, with an electron affinity more negative than that of the adjacent atoms: Xe and Te.

(d) $Z = 38$ 4. This is the element Sr, which has two $5s$ electrons. It is easier to remove one $5s$ electron than to remove the outermost $4s$ electron of Ca, but harder than removing the outermost $6s$ electron of Cs.

(e) $Z = 48$ 2. This is the element Cd. Its outer electron configuration is s^2 and thus it is diamagnetic.

(f) $Z = 20$ 2. This is the element Ca. Since its electron configuration is $[\mathrm{Ar}]4s^2$, all electrons are paired and it is diamagnetic.

47. Ga^{4+} and Ge^{5+} are unlikely to be found in chemical compounds because these ions are unstable. Atoms tend to gain or lose electrons such that they achieve a noble gas configuration. Removing 4 electrons from Ga and 5 from Ge does not give these atoms a noble gas configuration due to the electrons populating the 3d orbitals.

Integrative and Advanced Exercises

51. **(a)** Not possible. C (77 pm) and Ca^{2+}(100 pm) are very different in size; however the diagram requires these to be nearly the same size

(b) This is a possibility. Na^+ is approximately the same size as Sr (99 pm). Cl^- (181 pm) and Br^-(196 pm) are comparable, with one being slightly smaller.

(c) Not possible. There are three large atoms and only one small one. Y (165 pm), K (227 pm), Ca (197 pm), and the small Na^+ (99 pm).

(d) Not possible. The smaller atoms are of noticeably different sizes: Zr^{2+} (95 pm) and Mg^{2+} (72 pm).

(e) This is possible. Fe and Co are of comparable sizes (~125 pm), and Cs (265 pm) and Rb (248 pm) are comparable, with one being slightly smaller.

Thus, the answer is that both (b) and (e) are compatible with the sketch.

53. We can determine the atomic mass of indium by beginning with the atomic mass of oxygen, and using the chemical formula of InO to determine the amount (in moles) of indium in 100.0 g InO. In 100.0 g InO there is 82.5 g In and also 17.5 g O. $17.5\text{ g O}\times\frac{1\text{ mol O}}{16.0\text{ g O}}\times\frac{1\text{ mol In}}{1\text{ mol O}}=1.09\text{ mol In}$

$$\text{Atomic mass of In}=\frac{82.5\text{ g In}}{1.09\text{ mol In}}=75.7\text{ g In/mol}$$

With this value of the atomic mass of indium, Mendeleev might well have placed the element between As (75 g/mol) and Se (78 g/mol), that is, in his "Gruppe V" or "Gruppe VI."

55. **Al** Atomic radius usually decreases from left to right across a period and from bottom to top in a group. We expect the atomic radius of Al to be similar to that of Ge. Because Al is clearly more metallic than the metalloid Ge, the first ionization potential of Al is smaller than Ge.

In In is in the period below that of Ge and in the group to the left of that of Ge. Both of these locations predict a larger atomic radius for In than for Ge. In is clearly a metal, while Ge is a metalloid. The first ionization energy of In should be smaller than that of Ge.

Se Se is in the same period as Ge, but farther right. It should have a smaller atomic radius. Also because Se is to the right of Ge it should have a larger first ionization potential.

These predictions are summarized in the table below along with the values of the properties (in parentheses). The incorrect prediction is for the radius of Al. [But note that the radius of Al (143 pm) is larger than those of both B (88 pm) and Ga (122 pm). Clearly atomic radius does *not* increase uniformly down the family in Group 3A.]

Element	Atomic Radius, pm	First Ionization Energy, kJ/mol
Ge	123	762
Al	same (143)	same or smaller (578)
In	larger (150)	smaller (558)
Se	smaller (117)	larger (941)

57. We would assume the melting points and boiling points of interhalogen compounds to be the average of the melting and boiling points of the two elements that constitute them. (The melting point for bromine estimated in Practice Example 9-5A is 280 K. All other values used to determine the averages are actual values from Table 9.5 and Example 9-5.) The actual values to which these averages are compared are obtained from a handbook.

$$\text{BrCl melting point} = \frac{\text{Br}_2\ \text{m.p.} + \text{Cl}_2\ \text{m.p.}}{2} = \frac{280\ \text{K} + 172\ \text{K}}{2} = 226\ \text{K} \qquad \text{actual m.p.} = 207\ \text{K}$$

$$\text{boiling point} = \frac{\text{Br}_2\ \text{b.p.} + \text{Cl}_2\ \text{b.p.}}{2} = \frac{332\ \text{K} + 239\ \text{K}}{2} = 286\ \text{K} \qquad \text{actual b.p.} = 278\ \text{K}$$

$$\text{ICl melting point} = \frac{\text{I}_2\ \text{m.p.} + \text{Cl}_2\ \text{m.p.}}{2} = \frac{387\ \text{K} + 172\ \text{K}}{2} = 280\ \text{K} \qquad \text{actual m.p.} = 300.4\ \text{K}$$

$$\text{boiling point} = \frac{\text{I}_2\ \text{b.p.} + \text{Cl}_2\ \text{b.p.}}{2} = \frac{458\ \text{K} + 239\ \text{K}}{2} = 348\ \text{K} \qquad \text{actual b.p.} = 370.6\ \text{K}$$

At 25°C (298 K), BrCl is predicted to be a gas (which it is), while ICl is predicted to be a liquid (and it actually is a solid at 298 K, but it melts when the temperature is raised by just 2 K).

61. **(a)** A; Element "A" (Sr) has an electron configuration consistent with group 1A which are the alkali metals.

(b) B; Element "B" (Br) is a non-metal. It is easier for Br to gain an electron to form Br^- than for Sr to form Sr^-.

(c) A; Element "A" (Sr) has the larger atomic radius. In general, size decreases going across a period and increases going down a group. Since Sr has valence electrons in the higher energy 5s orbital, which is farther from the nucleus, Sr will be larger in size.

(d) B; Element "B" (Br) has the greatest electron affinity. Non-metals have a greater tendency to add electrons compared with metals.

62. Since (0.3734)(382) = 143 u, if we subtract 143 from 382 we get 239 u, which is very close to the correct value of 238 u.

First we convert to J/g°C: 0.0276×(4.184 J/cal) = 0.1155 J/g°C , so:
0.1155 = 0.011440 + (23.967/atomic mass); solving for atomic mass yields a value of 230 u, which is within about 3% of the correct value.

65. $$E_1 = \frac{-2^2 \times 2.179 \times 10^{-18}\ \text{J}}{1^2} = -8.716 \times 10^{-18}\ \text{J/atom}$$

This is the energy released when an electron combines with an alpha particle (He^{2+}) to the nucleus to form the ion He^+. The energy absorbed when the electron is removed from He^+, the ionization energy of He^+ or the *second* ionization energy of He, is the negative of this value. Then the energy per mole, E_m, is computed.

$$E_1 = E_1 \times N_A = \frac{8.716 \times 10^{-18}}{1\ \text{atom}} \times \frac{6.022 \times 10^{23}}{1\ \text{mol}} \times \frac{1\ \text{kJ}}{1000\text{J}} = 5249\ \text{kJ/mol}$$

This is in excellent agreement with the tabulated value of 5251 kJ/mol.

66. It should be relatively easy to remove electrons from ions of metallic elements, if the metal does not have a noble gas electron configuration. Thus, I_3 for Sc and I_2 for Ba should be small, with the second being smaller, since the electron is being removed from a more highly charged species in the case of I_3 for Sc. I_1 for F might be smaller than either of these because it involves removing only the first electron from a neutral atom, rather than removing an electron from a cation. There is some uncertainty here, because the electron being removed from F is not well shielded from the nuclear charge, and this value could be larger than the other two. The remaining ionization energies are both substantially larger than the other three because they both involve disrupting a noble gas electron configuration. I_3 for Mg is larger than I_2 for Na because it is more difficult to remove an electron from a more highly charged species. Literature values (in kJ/mol) are in parentheses in the following list.

I_1 for F (1681) ≈ I_2 for Ba (965) < I_3 for Sc (2389) < I_2 for Na (4562) < I_3 for Mg (7733)

Note that we have overestimated the difficulty of removing a second electron from a metal atom (I_2 for Ba) and underestimated the difficulty of removing the first electron from a small nonmetal atom (I_1 for F).

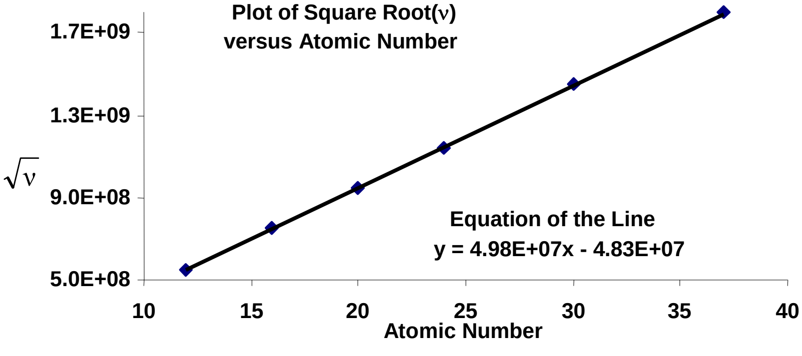
FEATURE PROBLEMS

70. The Moseley equation, $\nu = A(Z-b)^2$, where ν is the frequency of the emitted X-ray radiation, Z is the atomic number, and A and b are constants, relates the frequency of emitted X-rays to the nuclear charge for the atoms that make up the target of the cathode ray tube. X-rays are emitted by the element after one of its K-level electrons has been knocked out of the atom by collision with a fast moving electron. In this question, we have been asked to determine the values for the constants A and b. The simplest way to find these values is to plot $\sqrt{\nu}$ vs. Z. This plot provides $\sqrt{A}$ as the slope and $-\sqrt{A}$ (b) as the y –intercept. Starting with $\nu = A(Z-b)^2$, we first take the square root of both sides. This affords $\sqrt{\nu} = \sqrt{A}(Z - b)$. Multiplying out this expression gives $\sqrt{\nu} = \sqrt{A}(Z) - \sqrt{A}(b)$. This expression follows the equation of a straight line y = m*x* +b, where y = $\sqrt{\nu}$, m = $\sqrt{A}$, *x* = Z and b = $-\sqrt{A}$ (b). So a plot of $\sqrt{\nu}$ vs. Z will provide us with A and b, after a small amount of mathematical manipulation. Before we can construct the plot, we need to convert the provided X-ray wavelengths into their corresponding frequencies. For instance, Mg has an X-ray wavelength = 987 pm. The corresponding frequency for this radiation = c/λ, hence,

$$\nu = \frac{2.998 \times 10^{8}\ \text{m s}^{-1}}{9.87 \times 10^{-10}\ \text{m}} = 3.04 \times 10^{17}\ \text{s}^{-1}$$

Performing similar conversions on the rest of the data allows for the construction of the following table and plot (below).

(Z)	$\sqrt{\nu}$
12	5.51×10^{8}
16	7.48×10^{8}
20	9.49×10^{8}
24	1.14×10^{9}
30	1.45×10^{9}
37	1.80×10^{9}



The slope of the line is $4.98 \times 10^7 = \sqrt{A}$ and the y-intercept is $-4.83 \times 10^7 = -\sqrt{A}$ (b).
Thus, $A = 2.30 \times 10^{15}$ Hz and $b = \dfrac{-4.83 \times 10^7}{-4.98 \times 10^7} = 0.969$.

According to Bohr's theory, the frequencies that correspond to the lines in the emission spectrum are given by the equation: $(3.2881 \times 10^{15}\ \text{s}^{-1})\left(\dfrac{1}{(n_i)^2} - \dfrac{1}{(n_f)^2}\right)$,

where ($3.2881 \times 10^{15}\ \text{s}^{-1}$) represents the frequency for the lowest energy photon that is capable of completely removing (ionizing) an electron from a hydrogen atom in its ground state. The value of A (calculated in this question) is close to the Rydberg frequency ($3.2881 \times 10^{15}\ \text{s}^{-1}$), so it is probably the equivalent term in the Moseley equation. The constant b, which is close to unity, could represent the number of electrons left in the K shell after one K-shell electron has been ejected by a cathode ray. Thus, one can think of b as representing the screening afforded by the remaining electron in the K-shell. Of course screening of the nucleus is only be possible for those elements with $Z > 1$.

71. **(a)** The table provided in this question shows the energy changes associated with the promotion of the outermost valence electron of sodium into the first four excited states above the highest occupied ground state atomic orbital. In addition, we have been told that the energy needed to completely remove one mole of 3*s* electrons from one mole of sodium atoms in the ground state is 496 kJ. The ionization energy for each excited state can be found by subtracting the "energy quanta" entry for the excited state from 496 kJ mol^{-1}.

e.g., for [Ne]$3p^1$, the first ionization energy $= 496\ \dfrac{\text{kJ}}{\text{mol}} - 203\ \dfrac{\text{kJ}}{\text{mol}} = 293\ \dfrac{\text{kJ}}{\text{mol}}$

Thus, the rest of the ionization energies are:
[Ne]$4s^1$, = 496 kJ mol^{-1} – 308 kJ mol^{-1} = 188 kJ mol^{-1}
[Ne]$3d^1$, = 496 kJ mol^{-1} – 349 kJ mol^{-1} = 147 kJ mol^{-1}
[Ne]$4p^1$, = 496 kJ mol^{-1} – 362 kJ mol^{-1} = 134 kJ mol^{-1}

(b) Z_{eff} (the effective nuclear charge) for each state can be found by using the equation:

ionization energy in kJ mol^{-1} (I.E.) $= \dfrac{A(Z_{\text{eff}})^2}{n^2}$

Where n = starting principal quantum level for the electron that is promoted out of the atom and $A = 1.3121 \times 10^3$ kJ mol^{-1} (Rydberg constant).

For [Ne]$3p^1$ (n = 3) $\quad 2.93 \times 10^2\ \text{kJmol}^{-1} = \dfrac{1.3121 \times 10^3\ \dfrac{\text{kJ}}{\text{mol}}\ (Z_{\text{eff}})^2}{3^2} \quad Z_{\text{eff}} = 1.42$

For [Ne]$4s^1$ (n = 4) $\quad 1.88 \times 10^2\ \text{kJmol}^{-1} = \dfrac{1.3121 \times 10^3\ \dfrac{\text{kJ}}{\text{mol}}\ (Z_{\text{eff}})^2}{4^2} \quad Z_{\text{eff}} = 1.51$

$$\text{For [Ne]}3d^1 \text{ (n = 3)} \quad 1.47 \times 10^2 \text{ kJmol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{3^2} \quad Z_{\text{eff}} = 1.00$$

$$\text{For [Ne]}4p^1 \text{ (n = 4)} \quad 1.34 \times 10^2 \text{ kJmol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4^2} \quad Z_{\text{eff}} = 1.28$$

(c) $\bar{r}_{\text{nl}}$, which is the average distance of the electron from the nucleus for a particular orbital, can be calculated with the equation:

$$\bar{r}_{\text{nl}} = \frac{n^2 a_o}{Z_{eff}}\left(1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right)$$

Where a_o = 52.9 pm,
n = principal quantum number
ℓ = angular quantum number for the orbital

$$\text{For [Ne]}3p^1 \text{ (n = 3, } \ell = 1\text{)} \quad \bar{r}_{3p} = \frac{3^2(52.9 \text{ pm})}{1.42}\left(1+\frac{1}{2}\left(1-\frac{1(1+1)}{3^2}\right)\right) = 466 \text{ pm}$$

$$\text{For [Ne]}4s^1 \text{ (n = 4, } \ell = 0\text{)} \quad \bar{r}_{4s} = \frac{4^2(52.9 \text{ pm})}{1.51}\left(1+\frac{1}{2}\left(1-\frac{0(0+1)}{4^2}\right)\right) = 823 \text{ pm}$$

$$\text{For [Ne]}3d^1 \text{ (n = 3, } \ell = 2\text{)} \quad \bar{r}_{3d} = \frac{3^2(52.9 \text{ pm})}{1.00}\left(1+\frac{1}{2}\left(1-\frac{2(2+1)}{3^2}\right)\right) = 555 \text{ pm}$$

$$\text{For [Ne]}4p^1 \text{ (n = 4, } \ell = 1\text{)} \quad \bar{r}_{4p} = \frac{4^2(52.9 \text{ pm})}{1.28}\left(1+\frac{1}{2}\left(1-\frac{1(1+1)}{4^2}\right)\right) = 950 \text{ pm}$$

(d) The results from the Z_{eff} calculations show that the greatest effective nuclear charge is experienced by the 4*s* orbital (Z_{eff} = 1.51). Next are the two *p*-orbitals, 3*p* and 4*p*, which come in at 1.42 and 1.28 respectively. Coming in last is the 3*d* orbital, which has a Z_{eff} = 1.00. These results are precisely in keeping with what we would expect. First of all, only the *s*-orbital penetrates all the way to the nucleus. Both the *p*- and *d*-orbitals have nodes at the nucleus. Also *p*-orbitals penetrate more deeply than do *d*-orbitals. Recall that the more deeply an orbital penetrates (i.e., the closer the orbital is to the nucleus), the greater is the effective nuclear charge felt by the electrons in that orbital. It follows then that the 4*s* orbital will experience the greatest effective nuclear charge and that the Z_{eff} values for the 3*p* and 4*p* orbitals should be larger than the Z_{eff} for the 3*d* orbital.

The results from the $\bar{r}_{\text{nl}}$ calculations for the four excited state orbitals show that the largest orbital in the set is the 4*p* orbital. This is exactly as expected because the 4*p* orbital is highest in energy and hence, on average farthest from the nucleus. The 4*s* orbital has an average position closer to the nucleus because it experiences a larger effective nuclear charge. The 3*p* orbital, being lowest in energy and hence on average closest to the nucleus, is the smallest orbital in the set. The 3*p* orbital has an average position closer to the nucleus than the 3*d* orbital (which is in the same principal quantum level), because it penetrates more deeply into the atom.

SELF-ASSESSMENT EXERCISES

77. The answer is (b). The element in question is antimony (Sb), which is in the same group as Bi.

78. The answer is (a), K. This is because atomic radius decreases going from left to right of the period.

79. The answer is (a), Cl^-. All of the choices have the same electron configuration as Ar, but Cl^- has an extra electron in the valence shell, which expands the ionic radius.

80. The answer is (b), because it has the smallest radius (and highest electron affinity). Therefore, the valence electrons are held more tightly, hence a higher first ionization energy.

81. The answer is (a), Br. This is because electron affinities increase across the periodic table, and are greatest for nonmetallic main group elements. The other choices are for metals.

82. The answer is (d), Sr^{2+}. They both have the electron configuration of Kr.

83. The electron configurations of the first and second ionization products of Cs are as follows:
Cs^+: [Xe], or [Kr] $5s^24d^{10}5p^6$
Cs^{2+}: [Kr] $5s^24d^{10}5p^5$
The second ionization energy is much greater because one has to overcome the extra energy required to remove an electron from a stable, filled subshell (which resembles that of a stable noble atom Xe).

84. The first ionization energy of Mg is higher than Na because, in the case of Mg, an electron from a filled subshell is being removed, whereas in Na, the removing of one electron leads to the highly stable electron configuration of Ne. The second ionization of Mg is lower than Na, because in the case Mg, the electron configuration of Ar is achieved, whereas in Na, the stable [Ar] configuration is being lost by removing an electron from the filled subshell.

85. **(a)** As, because it is the left and bottom-most element in the choices given
(b) F^-. Xe valence shell has $n = 5$, so it would be the largest and therefore not correct. Among those with shells with n = 2, F^- is the smallest because it has the highest nuclear charge and therefore more attraction of the orbitals to the nucleus
(c) Cl^-, because it is the most electronegative, and is being farther removed from the ideal filled subshell electron configuration
(d) Carbon, because it is the smallest, and hence has the least amount of shielding of the nucleus from the valence band, and the greatest attraction between the valence electrons and the nucleus
(e) Carbon, because electron affinity increases going across a period

86. The trends would generally follow higher first ionization energy values for a fuller subshell. The exception is the case of S and P, where P has a slightly higher value. This is because there is a slight energy advantage to having a half-filled subshell with an electron in each of p_x, p_y and p_z orbitals as in the case of P, whereas the S has one extra electron.

87. The pairs are Ar/Ca, Co/Ni, Te/I and Th/Pa. The periodic table must be arranged by atomic number because only this order is consistent with the regularity in electron configurations that is the ultimate basis of the table.

88. **(a)** protons = 50
(b) neutrons = 69
(c) *4d* electrons = 10
(d) *3s* electrons = 2
(e) *5p* electrons = 2
(f) valence shell electrons = 4

89. **(a)** F; it is the top right-most reactive element and has the highest electron affinity
(b) Sc
(c) Si

90. **(a)** C
(b) Rb
(c) At

91. **(a)** Ba
(b) S
(c) Bi, because Ba<Ca<Bi<As<S

92. Rb>Ca>Sc>Fe>Te>Br>O>F

93. **(a)** False. The *s* orbitals have a higher probability of being near the nucleus (whereas the probability is zero for *p* and *d* orbitals), so they are more effective at shielding.
(b) True. The *s* orbitals have much better penetration than *p* or *d* orbitals and therefore are better at shielding nuclear charge.
(c) True for all atoms except hydrogen. Z_{eff} has a maximum theoretical value equal to Z. In practice, it is always less in a multi-electron atom, because there is always some shielding of the nuclear charge by the electrons.
(d) True. Electrons in *p* orbitals penetrate better than those in *d* orbitals.
(e) True. To understand this, remember that ionization energy, $I = R_H \times Z_{eff}^2 / n^2$. Use the data in Table 9-4 to determine Z_{eff} for these elements.

94. **(a)** False. The 1*s* orbital has more penetration with the nucleus than the 2*s* orbital, and feels nearly the entire charge of the nucleus (higher Z_{eff}).
(b) False. The Z_{eff} of a 2*s* orbital is greater than a 2*p* because of higher penetration.
(c) True, because the electron in an *s* orbital has greater penetration with the nucleus and is more tightly attracted.

(d) True. Because of the greater penetration of the 2*s* electrons, the 2*p* electrons are more effectively shielded from the full nuclear charge.

95. These ionization energies are the reverse of electron affinities, for example, *I* for Li^- is –(-59.6 kJ/mol). The variations in these anions follow those seen in Figure 9-11.

96. Ionization energy generally increases with Z for a given period (and decreases going to higher periods) with the exception of the small deviation observed going from N to O because N has a slightly more stable configuration for N where half of the orbitals are filled.