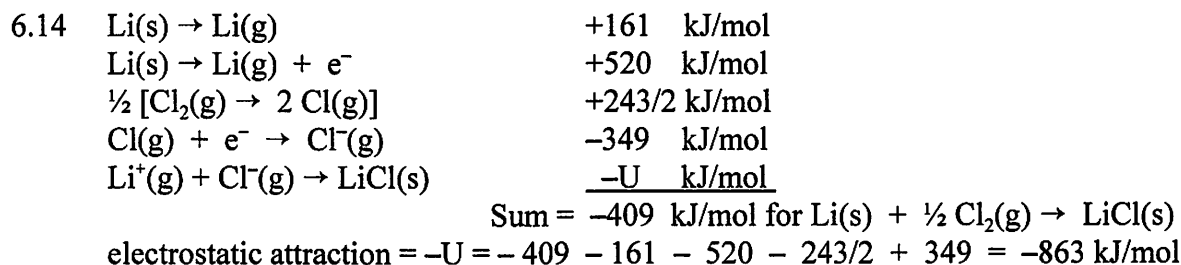
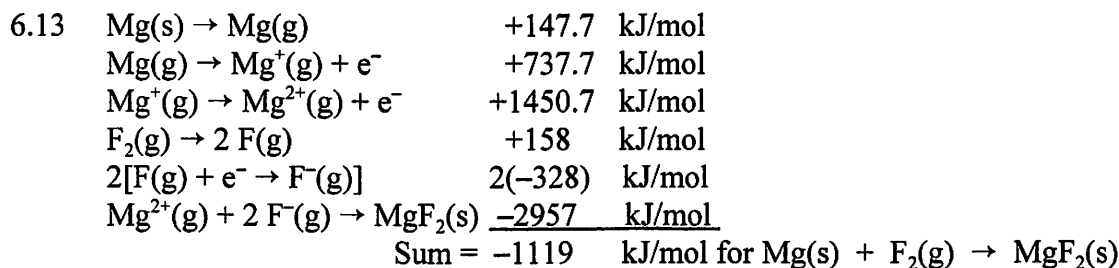


6

Ionic Compounds: Periodic Trends and Bonding Theory

- 6.1 (a) Ra^{2+} [Rn] (b) Ni^{2+} [Ar] $3d^8$ (c) N^{3-} [Ne]
- 6.2 (b) Ti^{4+} , Ca^{2+} , and Cl^- are isoelectronic. They all have the electron configuration of Ar.
(c) Na^+ , Mg^{2+} , and Al^{3+} are isoelectronic. They all have the electron configuration of Ne.
- 6.3 As the positive charge of an element increases, Z_{eff} increases and the size decreases. Fe is larger than both Fe^{2+} and Fe^{3+} .
- 6.4 K^+ , Ca^{2+} , and Cl^- are isoelectronic. The Z_{eff} for $\text{Ca}^{2+} > \text{K}^+ > \text{Cl}^-$.
In terms of size, $\text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$. Cl^- is yellow, K^+ is green, and Ca^{2+} is red.
- 6.5 Ionization energy generally increases from left to right across a row of the periodic table and decreases from top to bottom down a group. $\text{Rb} < \text{Se} < \text{O}$
- 6.6 (c) $<$ (b) $<$ (a) $<$ (d)
- 6.7 Be $1s^2 2s^2$; C $1s^2 2s^2 2p^2$; N $1s^2 2s^2 2p^3$
Be would have the larger third ionization energy because this electron would come from the 1s orbital.
- 6.8 The first 3 electrons are relatively easy to remove compared to the fourth and fifth electrons. The atom is Al.
- 6.9 Ge $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
As $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$
Br $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
As has the least favorable E_{ea} because you are adding an electron to a half-filled set of 4p orbitals, pairing one pair of electrons and increasing repulsion. Br has the most favorable E_{ea} because on adding an electron you are achieving an inert gas configuration. Adding an electron to Ge goes into an empty 4p orbital which is favorable (but not as favorable as Br) and E_{ea} for Ge is between that for As and Br.
least favorable As $<$ Ge $<$ Br most favorable.
- 6.10 The least favorable E_{ea} is for Kr (red) because it is a noble gas with a filled set of 4p orbitals. The most favorable E_{ea} is for Ge (blue) because the 4p orbitals would become half filled. In addition, Z_{eff} is larger for Ge than it is for K (green).
- 6.11 Sr in SrCO_3 is Sr^{2+} , $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

6.12 Group 6A elements will gain 2 electrons. The ion charge will be 2–.



6.15 Sr, Cu and Mg are 2+ cations. Cs is a large 1+ cation. I is a large 1– anion. F is a small 1– anion. O is a small 2– anion. Mg^{2+} is smaller than either Sr^{+2} or Cu^{2+} . Smaller ions with higher charges result in larger lattice energies. MgO has the largest lattice energy of the group.

6.16 The anions are larger than the cations. Cl^- is larger than O^{2-} because it is below it in the periodic table. Therefore, (a) is NaCl and (b) is MgO. Because of the higher ion charge and shorter cation–anion distance, MgO has the larger lattice energy.

6.17 (a), (c) and (d)

6.18 In ionic liquids the cation has an irregular shape and one or both of the ions are large and bulky to disperse charges over a large volume. Both factors minimize the crystal lattice energy, making the solid less stable and favoring the liquid.

6.19 (a) Iodide ions are larger than bromide ions. Tetraheptylammonium bromide corresponds to picture (ii) and tetraheptylammonium iodide corresponds to picture (i).
 (b) Tetraheptylammonium bromide has the larger lattice energy because bromide ions are smaller than iodide ions.
 (c) Tetraheptylammonium bromide has melting point of 88 °C and tetraheptylammonium iodide has a melting point of 39 °C.

6.20 (a) F^- , $1s^2 2s^2 2p^6$
 Se^{2-} , $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
 O^{2-} , $1s^2 2s^2 2p^6$
 Br^- , $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
 (b) F^- and O^{2-} are isoelectronic; Se^{2-} and Br^- are isoelectronic.
 (c) The larger Br^- .

Conceptual Problems

6.21

- (a) Al^{3+}
- (b) Cr^{3+}
- (c) Sn^{2+}
- (d) Ag^+

6.22 The first sphere gets larger on going from reactant to product. This is consistent with it being a nonmetal gaining an electron and becoming an anion. The second sphere gets smaller on going from reactant to product. This is consistent with it being a metal losing an electron and becoming a cation.

6.23

6.24 Ca (red) would have the largest third ionization energy of the three because the electron being removed is from a filled valence shell. For Al (green) and Kr (blue), the electron being removed is from a partially filled valence shell. The third ionization energy for Kr would be larger than that for Al because the electron being removed from Kr is coming out of a 4p orbital while the electron being removed from Al makes Al isoelectronic with Ne. In addition, Z_{eff} is larger for Kr than for Al. The ease of losing its third electron is $\text{Al} < \text{Kr} < \text{Ca}$.

6.25 The first 2 electrons are relatively easy to remove compared to the third and fourth electron. The atom is Mg.

6.26 (a) MgSO_4 (b) Li_2CO_3 (c) FeCl_2 (d) $\text{Ca}_3(\text{PO}_4)_2$

6.27 (a) shows an extended array, which represents an ionic compound.
(b) shows discrete units, which represent a covalent compound.

6.28 (a) I_2 (b) Na (c) NaCl (d) Cl_2

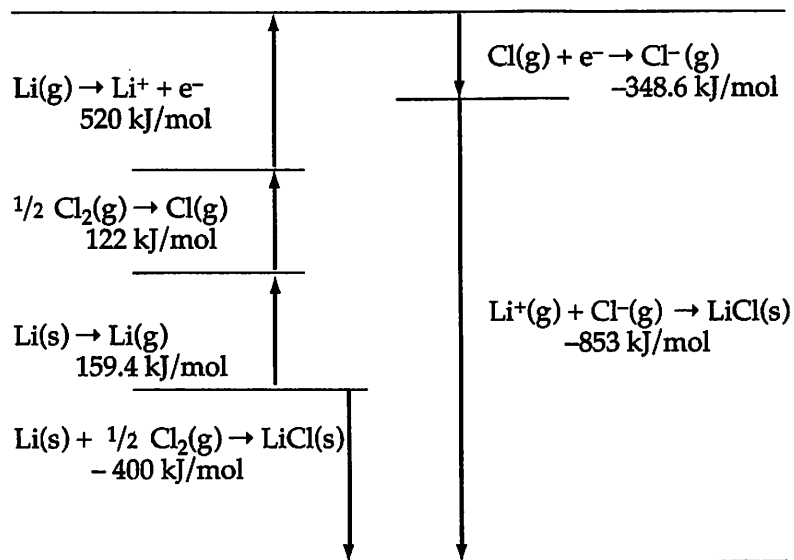
6.29 (c) has the largest lattice energy because the charges are closest together.
(a) has the smallest lattice energy because the charges are farthest apart.

Chapter 6 – Ionic Compounds: Periodic Trends and Bonding Theory

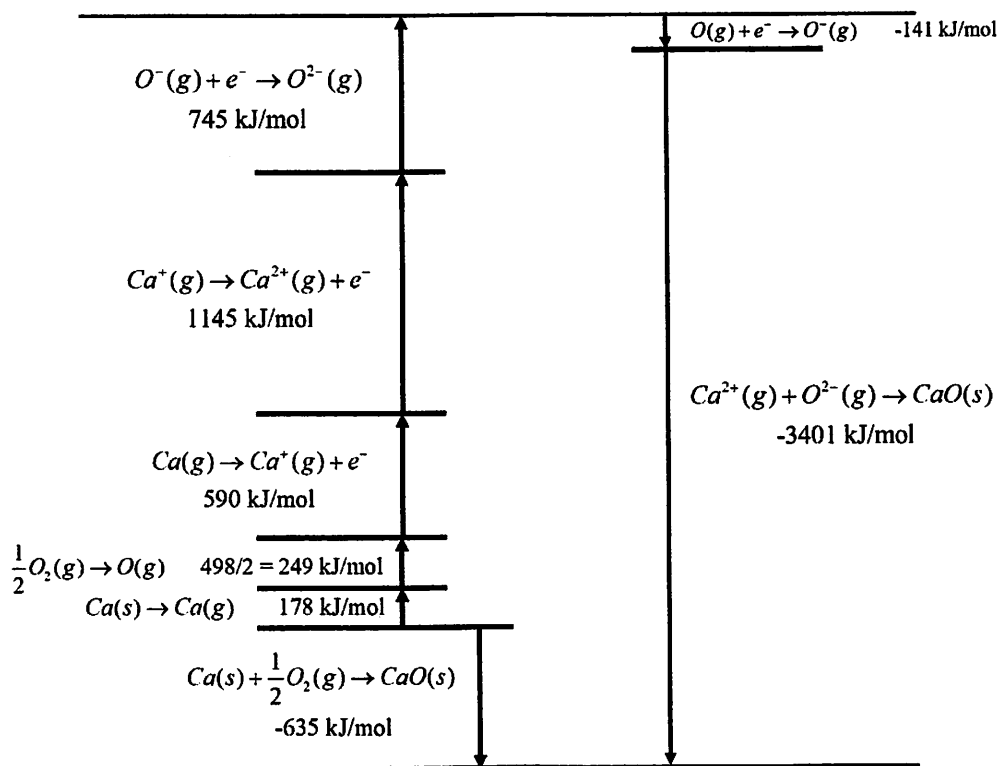
6.30 All the ions in both drawings are singly charged, so only the size of the ions is important. The ions in drawing (b) are smaller and closer together, so (b) has the larger lattice energy.

6.31 Green, CBr_4 ; Blue, SrF_2 ; Red, PbS or PbS_2

6.32



6.33



Section Problems

Electron Configuration of Ions (Section 6.1)

- 6.34 A covalent bond results when two atoms share several (usually two) of their electrons. An ionic bond results from a complete transfer of one or more electrons from one atom to another.
- 6.35 (a) and (d), covalent; (b) and (c), ionic
- 6.36 A molecule is the unit of matter that results when two or more atoms are joined by covalent bonds. An ion results when an atom gains or loses electrons.
- 6.37 (a), (b), and (d), ions; (c), molecule
- 6.38 (a) Be^{2+} , 4 protons and 2 electrons (b) Rb^{+} , 37 protons and 36 electrons
(c) Se^{2-} , 34 protons and 36 electrons (d) Au^{3+} , 79 protons and 76 electrons
- 6.39 (a) A $2+$ cation that has 36 electrons must have 38 protons. $X = \text{Sr}$.
(b) A $1-$ anion that has 36 electrons must have 35 protons. $X = \text{Br}$.
- 6.40 (a) La^{3+} , $[\text{Xe}]$ (b) Ag^{+} , $[\text{Kr}] 4d^{10}$ (c) Sn^{2+} , $[\text{Kr}] 5s^2 4d^{10}$
- 6.41 (a) Se^{2-} , $[\text{Kr}]$ (b) N^{3-} , $[\text{Ne}]$
- 6.42 Ca^{2+} , $[\text{Ar}]$; Ti^{2+} , $[\text{Ar}] 3d^2$
- 6.43 $Z = 30$, Zn
- 6.44 The neutral atom contains 12 e^{-} and is Mg. The ion is Mg^{2+} .
- 6.45 $[\text{Kr}] 4d^3$, Mo^{3+} ; $[\text{Kr}] 5s^2 4d^2$, Zr
- 6.46 Cr^{2+} $[\text{Ar}] 3d^4$ $\begin{array}{ccccc} \uparrow & \uparrow & \uparrow & \uparrow & _ \\ & & 3d & & \end{array}$
 Fe^{2+} $[\text{Ar}] 3d^6$ $\begin{array}{ccccc} \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ & & 3d & & \end{array}$
- 6.47 Fe^{3+} $[\text{Ar}] 3d^5$ $\begin{array}{ccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ & & 3d & & \end{array}$

Ionic Radii (Section 6.2)

- 6.48 (a) S^{2-} ; decrease in effective nuclear charge and an increase in electron-electron repulsions leads to the anion being larger.
(b) Ca; in Ca^{2+} electrons are removed from a larger valence shell and there is an increase in effective nuclear charge leading to the smaller cation.

- (c) O^{2-} ; decrease in effective nuclear charge and an increase in electron-electron repulsions leads to O^{2-} being larger.
- 6.49 (a) Rb; in Rb^+ the electron is removed from a larger valence shell and there is an increase in effective nuclear charge leading to the smaller cation.
 (b) N^{3-} ; decrease in effective nuclear charge and an increase in electron-electron repulsions leads to the anion being larger.
 (c) Cr^{3+} ; in Cr^{6+} electrons are removed from a larger valence shell and there is an increase in effective nuclear charge leading to Cr^{6+} being the smaller cation.
- 6.50 Sr^{2+} , Se^{2-} , Br^- , and Rb^+ are isoelectronic. The Z_{eff} for $Sr^{2+} > Rb^+ > Br^- > Se^{2-}$. The smallest ion has the largest Z_{eff} .
 Ions arranged from smallest to largest are $Sr^{2+} < Rb^+ < Br^- < Se^{2-}$.
- 6.51 Mg^{2+} , O^{2-} , F^- , and Na^+ are isoelectronic. The Z_{eff} for $Mg^{2+} > Na^+ > F^- > O^{2-}$. The smallest ion has the largest Z_{eff} .
 Ions arranged from smallest to largest are $Mg^{2+} < Na^+ < F^- < O^{2-}$.
- 6.52 Cu^+ has more electrons than Cu^{2+} and a lower Z_{eff} ; therefore Cu^+ has the larger ionic radius.
- 6.53 Fe^{2+} has more electrons than Fe^{3+} and a lower Z_{eff} ; therefore Fe^{2+} has the larger ionic radius.
- 6.54 $S^{2-} > Ca^{2+} > Sc^{3+} > Ti^{4+}$, Z_{eff} increases on going from S^{2-} to Ti^{4+} .
- 6.55 O^{2-} and F^- have a [Ne] electron configuration. Se^{2-} and Rb^+ have a [Kr] electron configuration. Se^{2-} and Rb^+ are larger than both O^{2-} and F^- . Se^{2-} (atomic # = 34) has a lower Z_{eff} than Rb^+ (atomic # = 37), therefore, Se^{2-} has the the largest radius.

Ionization Energy (Section 6.3)

- 6.56 The largest E_{il} are found in Group 8A because of the largest values of Z_{eff} .
 The smallest E_{il} are found in Group 1A because of the smallest values of Z_{eff} .
- 6.57 Fr would have the smallest ionization energy, and He would have the largest.
- 6.58 Using Figure 6.4 as a reference:
- | | Lowest E_{il} | Highest E_{il} |
|-----|-----------------|------------------|
| (a) | K | Li |
| (b) | B | Cl |
| (c) | Ca | Cl |
- 6.59 Using Figure 6.4 as a reference:
- (a) $Na < I < P$
 (b) $Sr < Mg < P$
 (c) $Cs < Ca < Se$

Higher Ionization Energies (Section 6.4)

- 6.60 (a) K [Ar] 4s¹ Ca [Ar] 4s²
Ca has the smaller second ionization energy because it is easier to remove the second 4s valence electron in Ca than it is to remove the second electron in K from the filled 3p orbitals.
(b) Ca [Ar] 4s² Ga [Ar] 4s² 3d¹⁰ 4p¹
Ca has the larger third ionization energy because it is more difficult to remove the third electron in Ca from the filled 3p orbitals than it is to remove the third electron (second 4s valence electron) from Ga.
- 6.61 Sn has a smaller fourth ionization energy than Sb because of a smaller Z_{eff} .
Br has a larger sixth ionization energy than Se because of a larger Z_{eff} .
- 6.62 (a) 1s² 2s² 2p⁶ 3s² 3p³ is P (b) 1s² 2s² 2p⁶ 3s² 3p⁶ is Ar (c) 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² is Ca
Ar has the highest E_{i2} . Ar has a higher Z_{eff} than P. The 4s electrons in Ca are easier to remove than any 3p electrons.
Ar has the lowest E_{i7} . It is difficult to remove 3p electrons from Ca, and it is difficult to remove 2p electrons from P.
- 6.63 (b) Cl has the highest E_{i1} and smallest E_{i4} .
- 6.64 The likely second row element is boron because it has three valence electrons. The large fourth ionization energy is from an inner shell 1s electron.
- 6.65 The likely second row element is beryllium because it has two valence electrons. The large third and fourth ionization energies are from inner shell 1s electrons.

Electron Affinity (Section 6.5)

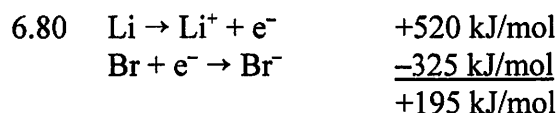
- 6.66 The relationship between the electron affinity of a univalent cation and the ionization energy of the neutral atom is that they have the same magnitude but opposite signs.
- 6.67 The relationship between the ionization energy of a univalent anion and the electron affinity of the neutral atom is that they have the same magnitude but opposite signs.
- 6.68 Na⁺ has a more negative electron affinity than either Na or Cl because of its positive charge.
- 6.69 Br would have a more negative electron affinity than Br⁻ because Br⁻ has no room in its valence shell for an additional electron.
- 6.70 Energy is usually released when an electron is added to a neutral atom but absorbed when an electron is removed from a neutral atom because of the positive Z_{eff} .
- 6.71 E_{i1} increases steadily across the periodic table from Group 1A to Group 8A because electrons are being removed from the same shell and Z_{eff} is increasing. The electron affinity increases irregularly from 1A to 7A and then falls dramatically for Group 8A because the additional electron goes into the next higher shell.

- 6.72 The electron-electron repulsion is large and Z_{eff} is low.
- 6.73 The 3p orbitals in P are half-filled. The electron affinity for Si is more negative because the added electron is going into an empty 3p orbital. The electron affinity for S is more negative because of a higher Z_{eff} .

Octet Rule (Section 6.6)

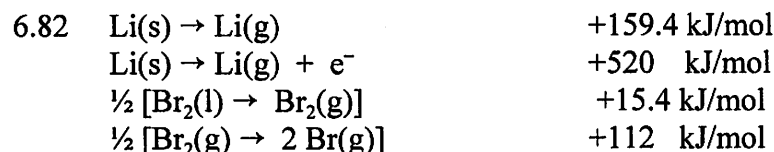
- 6.74 (a) [Ne], N^{3-} (b) [Ar], Ca^{2+} (c) [Ar], S^{2-} (d) [Kr], Br^-
- 6.75 (a) [Xe], I^- (b) [Ne], O^{2-} (c) [Ne], Al^{3+} (d) [Ar], Ca^{2+}
- 6.76 (a) Mg^{2+} and Cl^- , MgCl_2 , magnesium chloride
 (b) Ca^{2+} and O^{2-} , CaO , calcium oxide
 (c) Li^+ and N^{3-} , Li_3N , lithium nitride
 (d) Al^{3+} and O^{2-} , Al_2O_3 , aluminum oxide
- 6.77 (a) Na^+ and I^- , NaI , sodium iodide
 (b) K^+ and S^{2-} , K_2S , potassium sulfide
 (c) Li^+ and N^{3-} , Li_3N , lithium nitride
 (d) Ba^{2+} and F^- , BaF_2 , barium fluoride
- 6.78 (a) Because X reacts by losing electrons, it is likely to be a metal.
 (b) Because Y reacts by gaining electrons, it is likely to be a nonmetal.
 (c) X_2Y_3
 (d) X is likely to be in group 3A and Y is likely to be in group 6A.
- 6.79 (a) Because X reacts by losing electrons, it is likely to be a metal.
 (b) Because Y reacts by gaining electrons, it is likely to be a nonmetal.
 (c) XY_2
 (d) X is likely to be in group 2A and Y is likely to be in group 7A.

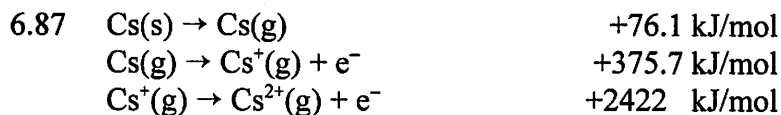
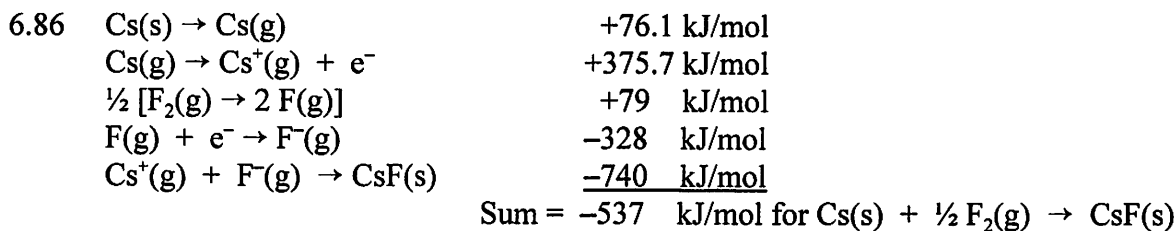
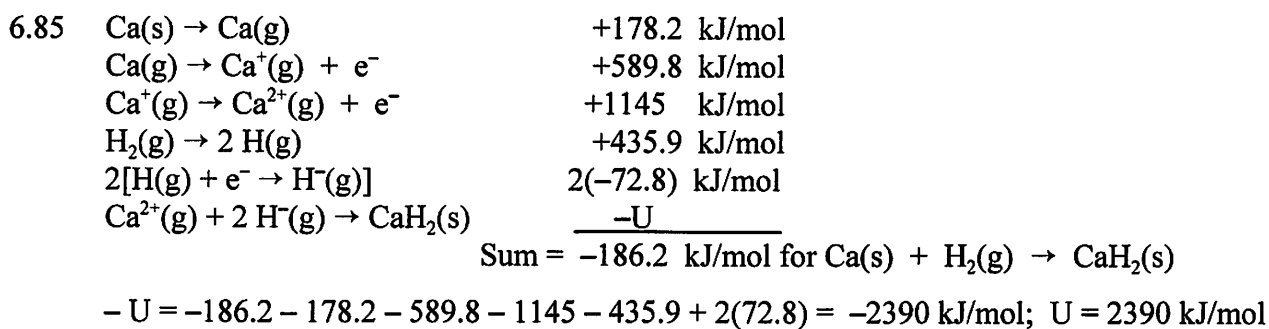
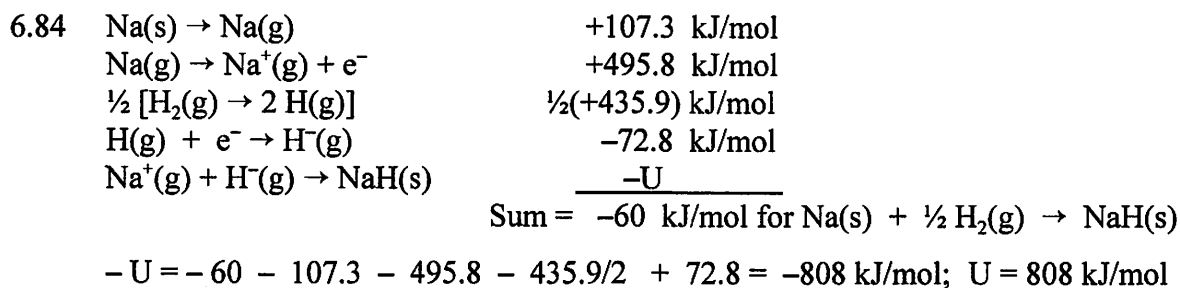
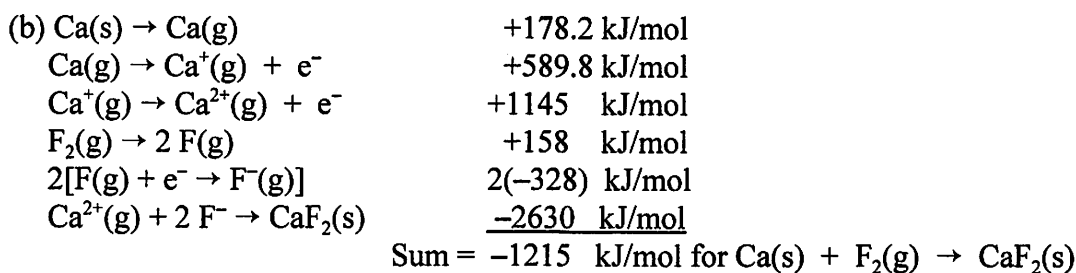
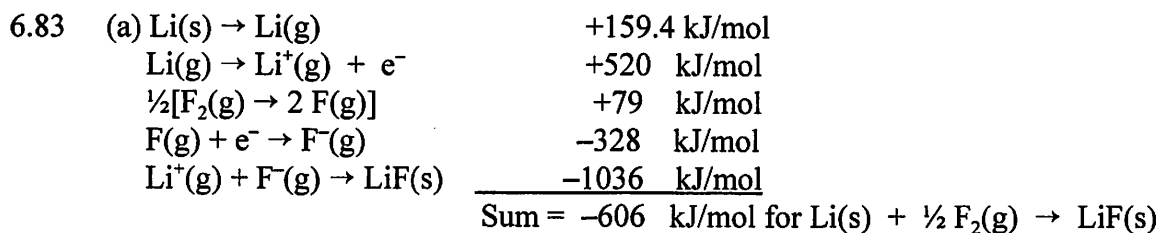
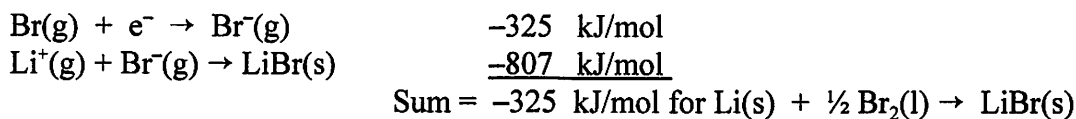
Formation of Ionic Compounds (Section 6.7)

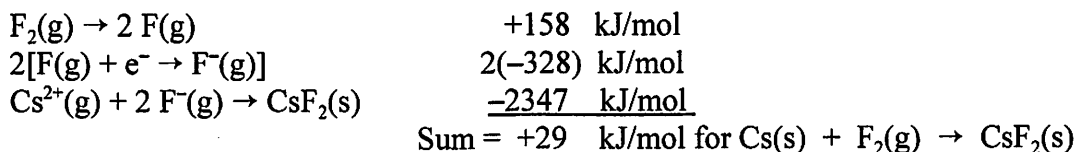


The total energy = +195 kJ/mol, which is unfavorable because it is positive.

- 6.81 The total energy = (376 kJ/mol) + (-349 kJ/mol) = +27 kJ/mol, which is unfavorable because it is positive.

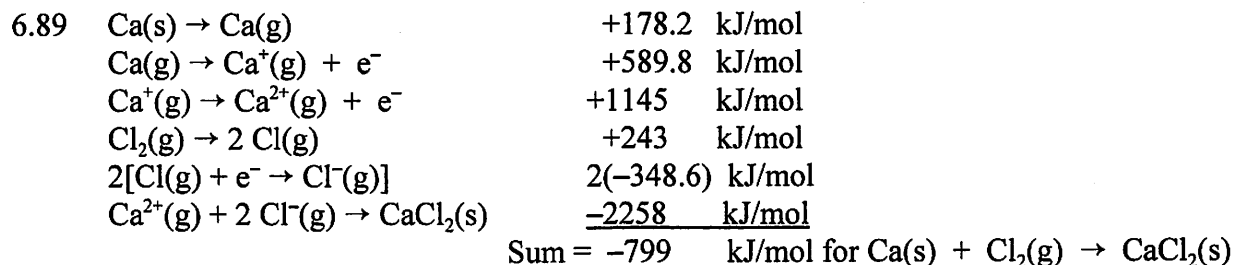
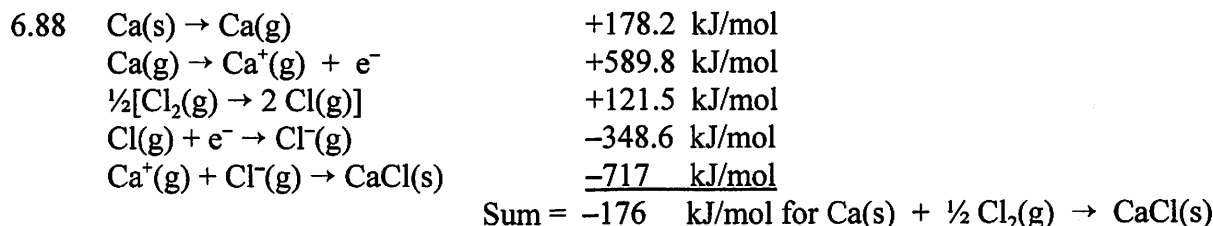




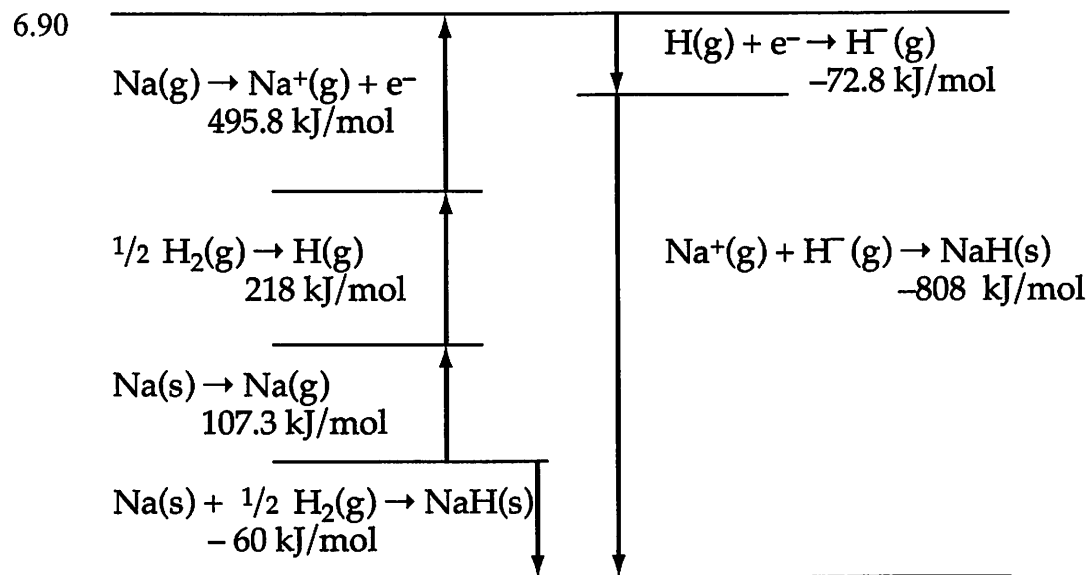


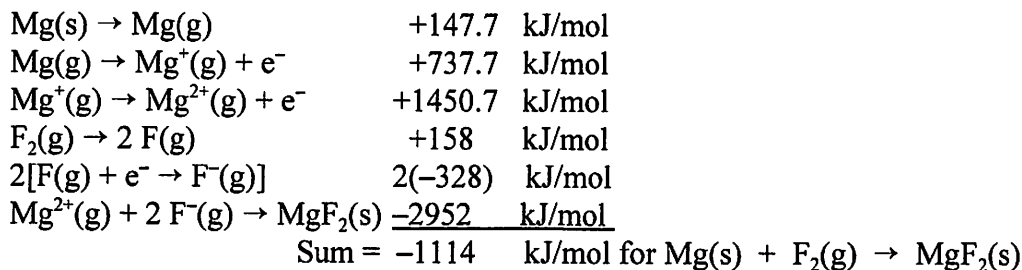
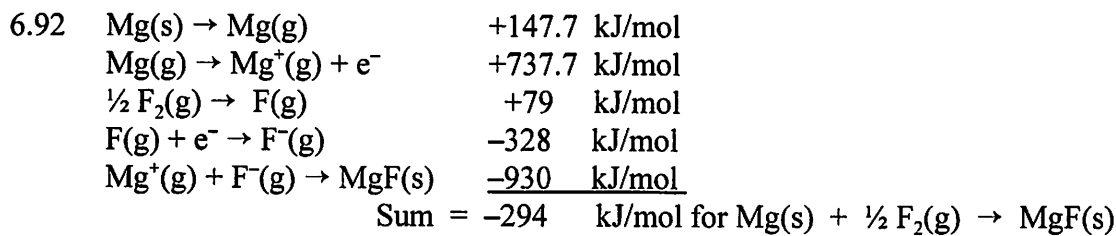
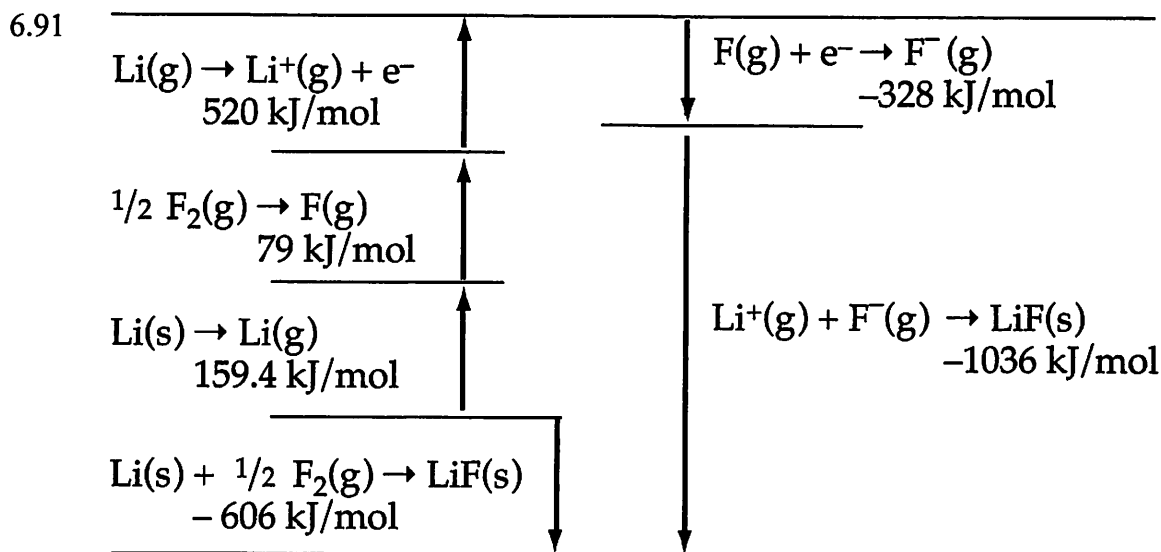
The overall reaction absorbs 29 kJ/mol.

In the reaction of cesium with fluorine, CsF will form because the overall energy for the formation of CsF is negative, whereas it is positive for CsF₂.



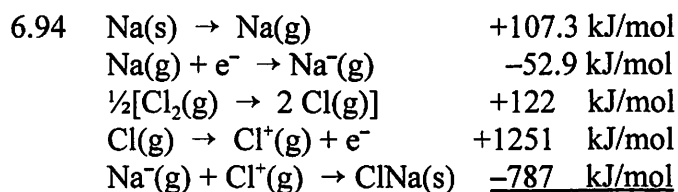
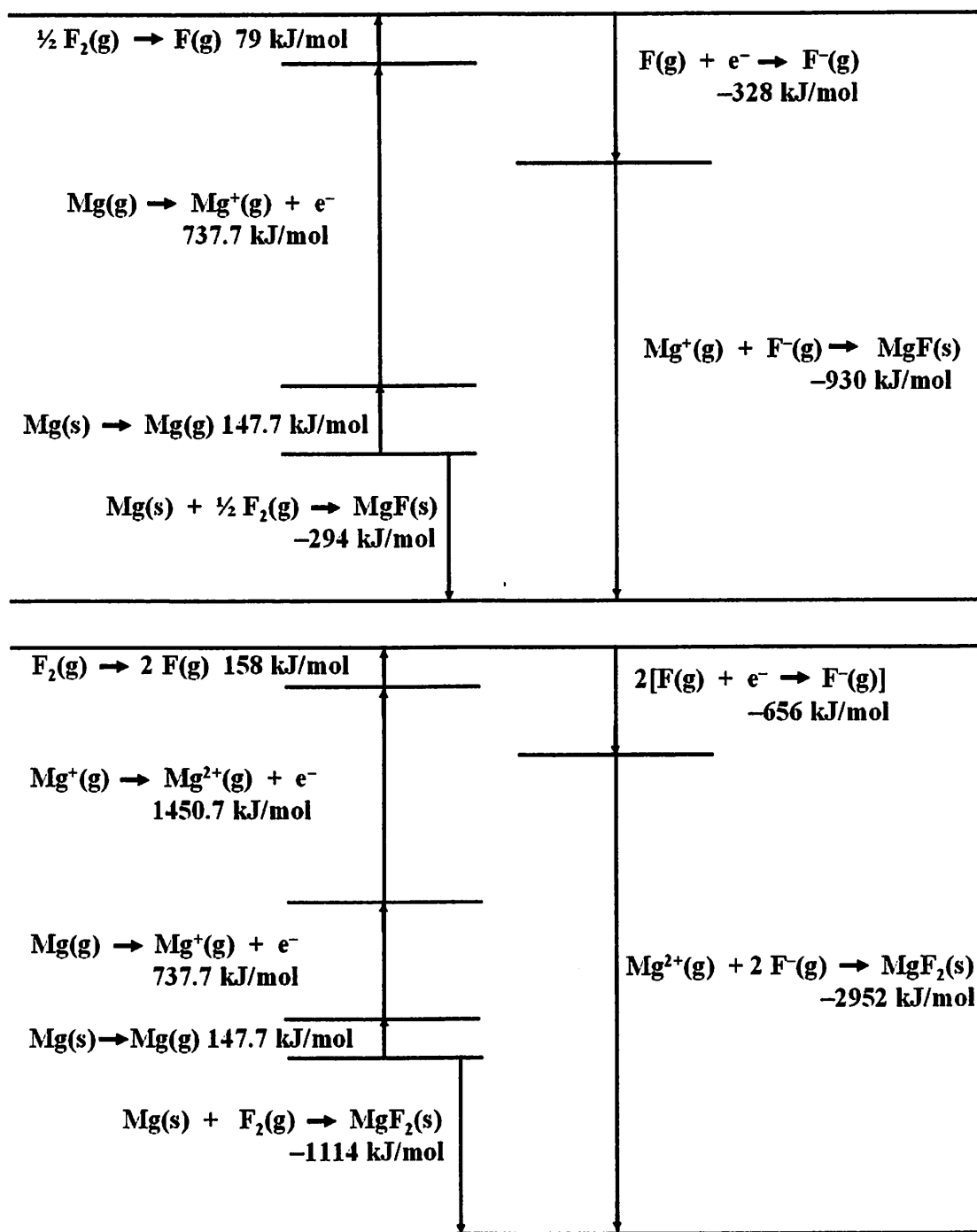
In the reaction of calcium with chlorine, CaCl₂ will form because the overall energy for the formation of CaCl₂ is much more negative than for the formation of CaCl.





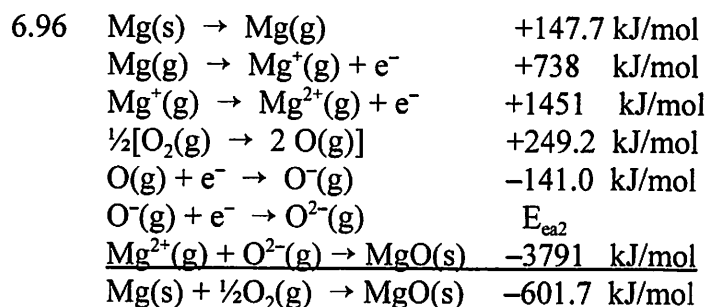
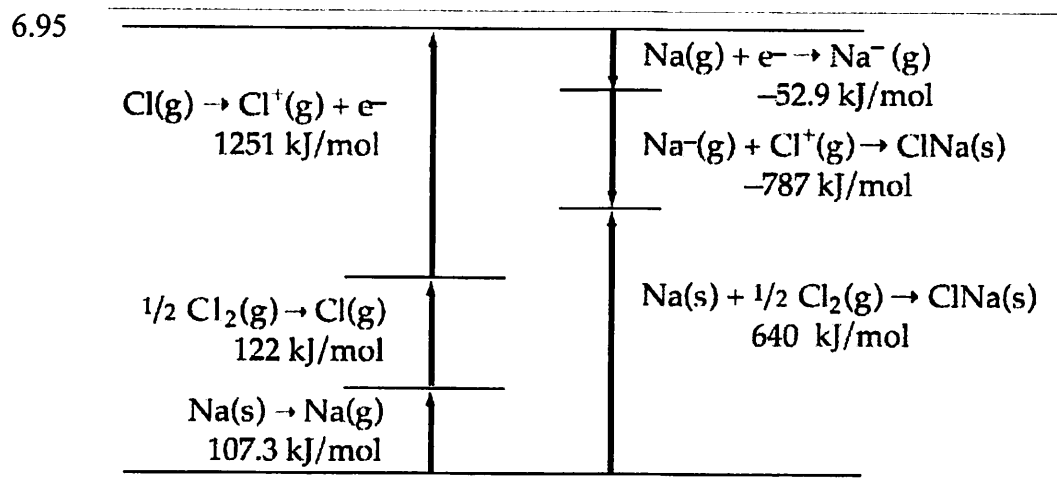
In the reaction of magnesium with fluorine, MgF_2 will form because the overall energy for the formation of MgF_2 is much more negative than for the formation of MgF .

6.93



$$\text{Sum} = +640 \text{ kJ/mol for } \text{Na}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}^+\text{Na}^-(\text{s})$$

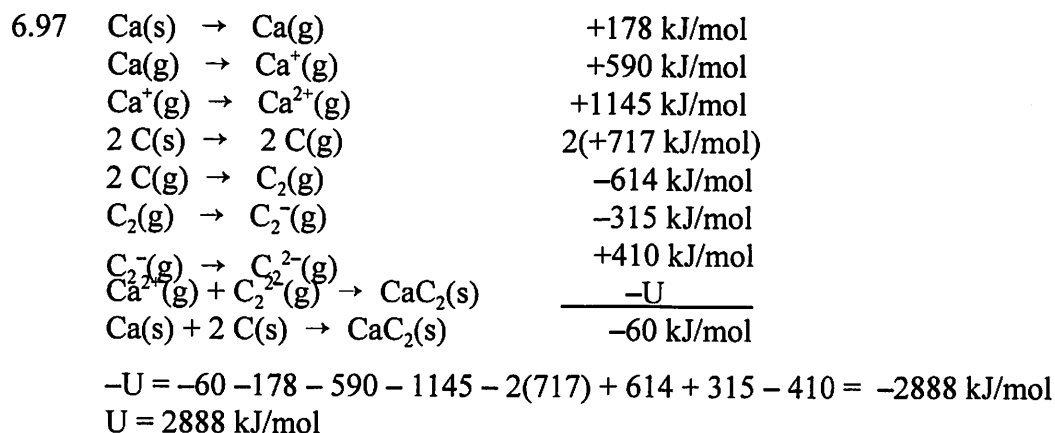
The formation of Cl^+Na^- from its elements is not favored because the net energy change is positive whereas it is negative for the formation of Na^+Cl^- .



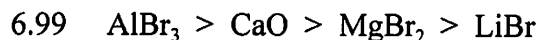
$$147.7 + 738 + 1451 + 249.2 - 141.0 + E_{\text{ea2}} - 3791 = -601.7$$

$$E_{\text{ea2}} = -147.7 - 738 - 1451 - 249.2 + 141.0 + 3791 - 601.7 = +744 \text{ kJ/mol}$$

Because E_{ea2} is positive, O^{2-} is not stable in the gas phase. It is stable in MgO because of the large lattice energy that results from the +2 and -2 charge of the ions and their small size.



Lattice Energy (Section 6.8)



Multiconcept Problems

6.100 When moving diagonally down and right on the periodic table, the increase in atomic radius caused by going to a larger shell is offset by a decrease caused by a higher Z_{eff} . Thus, there is little net change in the charge density.

6.101 (a) Assume a 100.0 g sample. From the percent composition data, a 100.0 g sample contains 57.67 g Cs and 42.33 g Pt.

$$57.67 \text{ g Cs} \times \frac{1 \text{ mol Cs}}{132.9 \text{ g Cs}} = 0.4339 \text{ mol Cs}$$

$$42.33 \text{ g Pt} \times \frac{1 \text{ mol Pt}}{195.1 \text{ g Pt}} = 0.2170 \text{ mol Pt}$$

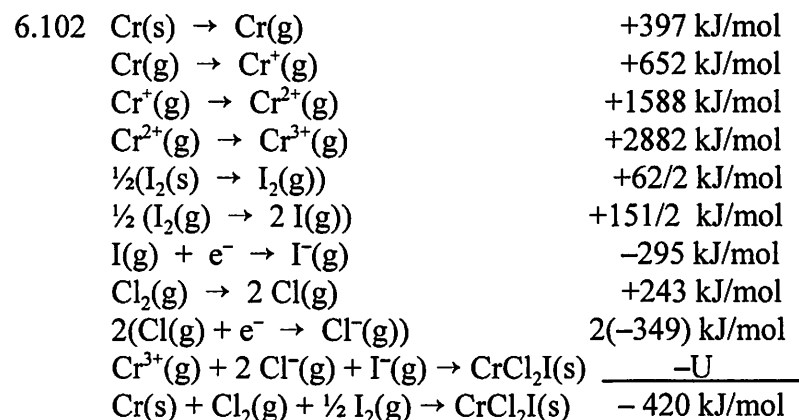
$\text{Cs}_{0.4339}\text{Pt}_{0.2170}$; divide each subscript by the smaller, 0.2170.

$$\text{Cs}_{0.4339 / 0.2170} \text{Pt}_{0.2170 / 0.2170}$$

The empirical formula is Cs_2Pt .

(b) Cs^+ , [Xe]

(c) Pt^{2-} , [Xe] $6s^2 4f^{14} 5d^{10}$



$$-U = -420 - 397 - 652 - 1588 - 2882 - 62/2 - 151/2 + 295 - 243 + 2(349) = -5295.5 \text{ kJ/mol}$$

$$U = 5295 \text{ kJ/mol}$$

6.103 (a) $E = (703 \text{ kJ/mol})(1000 \text{ J/1 kJ}) / (6.022 \times 10^{23} \text{ photons/mol}) = 1.17 \times 10^{-18} \text{ J/photon}$

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.17 \times 10^{-18} \text{ J}} = 1.70 \times 10^{-7} \text{ m} = 170 \times 10^{-9} \text{ m} = 170 \text{ nm}$$

(b) Bi [Xe] $6s^2 4f^{14} 5d^{10} 6p^3$

Bi⁺ [Xe] $6s^2 4f^{14} 5d^{10} 6p^2$

(c) $n = 6, l = 1$

(d) Element 115 would be directly below Bi in the periodic table. The valence electron is farther from the nucleus and less strongly held than in Bi. The ionization energy for element 115 would be less than that for Bi.

6.104 (a) Fe [Ar] 4s²3d⁶

Fe²⁺ [Ar] 3d⁶

Fe³⁺ [Ar] 3d⁵

(b) A 3d electron is removed on going from Fe²⁺ to Fe³⁺. For the 3d electron, n = 3 and l = 2.

$$(c) E(\text{J/photon}) = 2952 \text{ kJ/mol} \times \frac{1 \text{ mol photons}}{6.022 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 4.90 \times 10^{-18} \text{ J/photon}$$

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{4.90 \times 10^{-18} \text{ J}} = 4.06 \times 10^{-8} \text{ m} = 40.6 \times 10^{-9} \text{ m} = 40.6 \text{ nm}$$

(d) Ru is directly below Fe in the periodic table and the two metals have similar electron configurations. The electron removed from Ru to go from Ru²⁺ to Ru³⁺ is a 4d electron. The electron with the higher principal quantum number, n = 4, is farther from the nucleus, less tightly held, and requires less energy to remove.

6.105 (a) 58.4 nm = 58.4 × 10⁻⁹ m

$$E(\text{photon}) = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times \frac{3.00 \times 10^8 \text{ m/s}}{58.4 \times 10^{-9} \text{ m}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} = 2050 \text{ kJ/mol}$$

$$E_K = E(\text{electron}) = \frac{1}{2}(9.109 \times 10^{-31} \text{ kg})(2.450 \times 10^6 \text{ m/s})^2 \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \left(\frac{6.022 \times 10^{23}}{\text{mol}} \right)$$

$$E_K = 1646 \text{ kJ/mol}$$

$$E(\text{photon}) = E_i + E_K; \quad E_i = E(\text{photon}) - E_K = 2050 - 1646 = 404 \text{ kJ/mol}$$

(b) 142 nm = 142 × 10⁻⁹ m

$$E(\text{photon}) = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times \frac{3.00 \times 10^8 \text{ m/s}}{142 \times 10^{-9} \text{ m}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} = 843 \text{ kJ/mol}$$

$$E_K = E(\text{electron}) = \frac{1}{2}(9.109 \times 10^{-31} \text{ kg})(1.240 \times 10^6 \text{ m/s})^2 \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \left(\frac{6.022 \times 10^{23}}{\text{mol}} \right)$$

$$E_K = 422 \text{ kJ/mol}$$

$$E(\text{photon}) = E_i + E_K; \quad E_i = E(\text{photon}) - E_K = 843 - 422 = 421 \text{ kJ/mol}$$