Feature Problems 107. X = oxygen (16 u); nitryl fluoride has 2 atoms of O per molecule, nitrosyl fluoride, 1 atom of O; thionyl fluoride, 1 atom of O; and sulfuryl fluoride, 2 atoms of O. **108. (a)** N_2 from liquid air contains some Ar. **(b)** N_2 from liquid air has the greater density because the molecular mass of Ar is greater than that of N_2. **(c)** Mg reacts with N_2 but not with Ar, thus leaving pure residual Ar(g). **(d)** 0.50%

CHAPTER 7

Practice Examples 1A. 32.7 kJ **1B.** 4.89 kJ **2A.** 3.0×10^2 g **2B.** 37.9°C **3A.** -3.83×10^3 kJ/mol **3B.** 6.26 kJ/°C **4A.** $q_{rxn} = -65.2$ kJ/mol **4B.** 33.4°C **5A.** −114 J (work is done by the system) **5B.** +14.6 kJ (work is done on the system) **6A.** +1.70 × 10² J **6B.** 179 J of work done by system. **7A.** 60.6 g **7B.** 0.15 kJ of heat evolved **8A.** 3.31 kJ absorbed **8B.** 1.72 kg $H_2O(s)$ **9A.** $\Delta H° = -124$ kJ **9B.** $\Delta H° = -2006$ kJ/mol $CH_3CHOHCH_3(l)$ **10A.** 6 C(graphite) + 13/2 $H_2(g)$ + $O_2(g)$ + 1/2 $N_2(g) \longrightarrow C_6H_{13}O_2N(s)$ **10B.** twice the negative of the value in Table 7.2: $\Delta H° = +92.22$ kJ **11A.** $\Delta H° = -1367$ kJ/mol $C_2H_5OH(l)$ **11B.** $\Delta H° = -2.5 \times 10^3$ kJ/mol fuel **12A.** −1273 kJ/mol $C_6H_{12}O_6(s)$ **12B.** −184 kJ/mol $CH_3OCH_3(g)$ **13A.** $\Delta H° = -112.3$ kJ/mol AgI(s) **13B.** $\Delta H_f° = -505.8$ kJ/mol $Ag_2CO_3(s)$

Exercises 1. (a) $+2.9 \times 10^2$ kJ **(b)** −177 kJ **3. (a)** Zn: 0.385 J g^{-1} °C^{-1} **(b)** Pt: 0.13 J g^{-1} °C^{-1} **(c)** Al: 0.905 J g^{-1}°C^{-1} **5.** 5.4×10^2 °C **7.** 24.0°C **9.** 2.3×10^2 J mol^{-1} °C^{-1} **11.** -2.49×10^5 kJ **13. (a)** 65.59 kJ **(b)** 3.65×10^3 kJ; **(c)** 1.45×10^3 kJ **15. (a)** 504 kg **(b)** -6.20×10^5 kJ **(c)** 2.90×10^3 L **17.** 1.36×10^3 kJ **19. (a)** -5×10^1 kJ/mol KOH **(b)** Use more solute and less water to increase ΔT to three significant figures. **21.** 4.2×10^2 g **23.** −56 kJ/mol H_2O **25.** 39.6 g ice **27.** 2 g $H_2O(g)$ **29.** 4.98 kJ/°C **31. (a)** $q_{combustion} = -2.34 \times 10^3$ kJ/mol $C_5H_{10}O_5$ **(b)** $C_5H_{10}O_5(g) + 5 O_2(g) \longrightarrow$ $5 CO_2(g) + 5 H_2O(l)$ $\Delta H = -2.34 \times 10^3$ kJ **33. (a)** endothermic **(b)** +18 kJ/mol KCl **35.** 7.72 kJ/°C **37.** 5.23°C **39. (a)** −3.4 L atm **(b)** -3.5×10^2 J **(c)** −83 cal **41.** No work is done; nothing has been moved. **43. (a)** No pressure-volume work done. **(b)** $\Delta n_{gas} = -1$ mol: work is done on system by the surroundings. **(c)** $\Delta n_{gas} = +1$ mol: work is done on the surroundings by the system. **45. (a)** 0 J **(b)** −562 J **(c)** 0.08 kJ **47. (a)** yes, gas does work (w = negative). **(b)** yes, gas absorbs heat energy so that $q = -w$ **(c)** temperature of the gas stays the same **(d)** $\Delta U = 0$ (temperature is constant). **49.** impossible: The isothermal expansion of an ideal gas has $\Delta U = 0$ **51. (c)** **53. (a)** $\Delta U - 2008$ kJ/mol **(b)** $\Delta H = -2012$ kJ/mol **55.** $\Delta H° = 30.74$ kJ **57.** $\Delta H° = 290.$ KJ **59.** $\Delta H° = -217.5$ kJ **61.** $\Delta H° = -747.5$ kJ **63.** $\Delta H° = -35.8$ kJ **65. (a)** $\Delta H° = -55.7$ kJ **(b)** $\Delta H° = -1124$ kJ **67.** $\Delta H_f° = -206.0$ kJ/mol ZnS(s) **69.** $\Delta H° = +202.4$ kJ **71.** $\Delta H° = -1367$ kJ
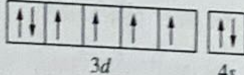
73. $\Delta H_f° = -102.9$ kJ/mol $CCl_4(g)$ **75.** $\Delta H° = -55$ kJ **77.** 2.40×10^6 kJ **Integrative and Advanced Exercises 80.** 3.5°C **81.** -1.95×10^3 kJ/mol $C_6H_8O_7$ **87.** Sewage gas produces more heat per liter at STP than coal gas **90.** 69.1% efficient **91.** 303 g $C_6H_{12}O_6$ **93.** 87.0% CH_4, 13.0% C_2H_6 (by volume) **96.** $C_2H_6O(g) + 3 O_2(g) \longrightarrow$ $2 CO_2(g) + 3 H_2O(l)$, $\Delta H° = -1.45 \times 10^3$ kJ **97.** 69 s **98.** −12 J

Feature Problems 105. (a) 45.0 mL of 1.00 M NaOH(aq) and 15.0 mL of 1.00 M citric acid **(b)** An excess reactant in a constant reaction volume would mean that less than the maximum amount of heat would be released, leading to a lower temperature attained. **(c)** $H_3C_6H_5O_7(aq) + 3 OH^-(aq) \longrightarrow$ $3 H_2O(l) + C_6H_5O_7^{3-}(aq)$ **108. (a)** about −147 J **(b)** total work done is the sum of the areas of the 11 rectangles under the P-V curve **(c)** maximum work = −152 J **(d)** maximum work of compression is for a one-step compression at 2.40 atm, i.e., 209 J; minimum work is the negative of (c), +152 J **(e)** $\Delta U = 0$; value of q is the negative of the work found in (d) **(f)** The value of q/T for the process in (c) is ΔS, the change in the state function, entropy (S), introduced in Chapter 19.

CHAPTER 8

Practice Examples 1A. 4.34×10^{14} Hz **1B.** 3.28 m **2A.** 410 to 520 kJ/mol **2B.** 4.612×10^{14} Hz (orange), 6.662×10^{14} Hz (indigo). We see the reflected color, principally green. **3A.** Yes, it is for $n = 9$, that is, $E_9 = -2.69 \times 10^{-20}$ J **3B.** no **4A.** 486.2 nm **4B.** 121.6 nm or 1216 Å **5A.** 80.13 nm **5B.** Be^{3+} **6A.** 1.21×10^{-43} m **6B.** 3.96×10^4 km/s **7A.** 6.4×10^{-43} m **7B.** 1.3 m/s **8A.** yes **8B.** $\ell = 2$ or 1 **9A.** 3p **9B.** $n = 3$; $\ell = 2, 1,$ or 0; $m_\ell = 2, 1, 0, -1,$ or −2 **10A.** Ti **10B.** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$; ten 3d electrons; one unpaired electron.

11A. Fe: [Ar]

↿⇂	↿	↿	↿	↿		↿⇂

3d   4s

11B.

Bi: [Xe]

↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂

4f

↿⇂	↿⇂	↿⇂	↿⇂	↿⇂		↿⇂		↿	↿	↿

5d   6s   6p

12A. (a) 5 **(b)** 6 **(c)** 0 **(d)** 2 **12B. (a)** 10 **(b)** 2 **(c)** 1 **Exercises 1.** 4.48 nm **3. (a)** and **(d)** are true **5. (c)** **7.** 8.3 min **9. (a)** 6.9050×10^{14} s^{-1}; **(b)** 397.11 nm; **(c)** $n = 10$ **11. (a)** 5.71×10^{-18} J/photon; **(b)** 61.1 kJ/mol **13.** $\Delta E = -1.550 \times 10^{-19}$ J; 2.339×10^{14} s^{-1} **15.** 656.46 nm, 486.26 nm, 434.16 nm, 410.28 nm **17.** $n = 8$ **19. (a)** 4.19×10^{-19} J/photon; **(b)** 252 kJ/mol **21. (b)** has the greatest energy and **(d)** has the least energy **23.** The radiation has $\nu = 3.03 \times 10^{16}$ s^{-1} and is in the ultraviolet region. **25. (a)** 6.60×10^{-19} J/photon; **(b)** ultraviolet yes, not infrared **27. (a)** 1.9 nm; **(b)** -6.053×10^{-20} J **29. (a)** 1.384×10^{14} s^{-1}; **(b)** 2166 nm; **(c)** infrared **31. (a)** 8.5×10^{-10} m

(b) no orbit at 4.00 Å; **(c)** $n = 8$, energy is -3.405×10^{-20} J (relative to $E_\infty = 0$ J); **(d)** No 2.50×10^{-17} J is not an allowed energy level. **33.** $n = 7$ to $n = 4$ **35. (a)** Line A: $n = 3$ to $n = 1$, Line B: $n = 4$ to $n = 1$ **(b)** H atom **37. (a)** Line A: $n = 5$ to $n = 2$, Line B: $n = 6$ to $n = 2$ **(b)** Be^{3+} ion **39.** Electrons **41.** 9.79×10^{-35} m **43.** The electron's position and velocity are both exactly known in the Bohr theory. This is not allowed by the Heisenberg uncertainty principle **45.** 1×10^{-13} m **47.** 1.4×10^7 m s^{-1} **49.** 17 cm **51.** 16 inches **53.** Discrete orbits in the Bohr atom versus regions of high electron probability in the wave mechanical atom. Both theories give the same value of the most probable distance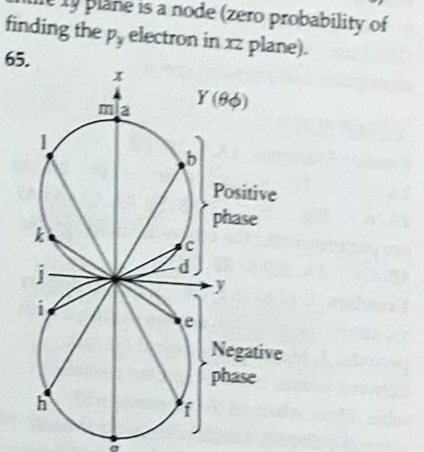 of the electron from the nucleus. **55. (c)** **57. (a)** 5p; **(b)** 4d; **(c)** 2s **59. (a)** one; **(b)** two; **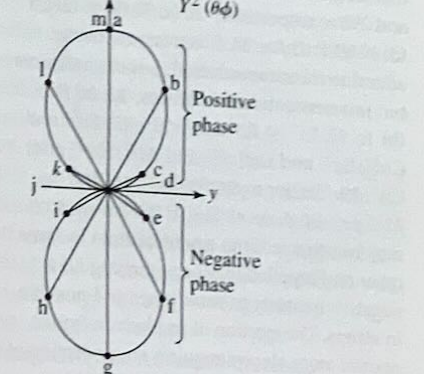(c)** ten; **(d)** eighteen; **(e)** five **61.** 106 pm **63.** For $2p_y$ wavefunction is $Y(\theta, \phi)_{py} = (0.75\pi)^{1/2} \sin \theta \sin \phi$, for all points in the xz plane, $\mu = 0$, and since $\sin 0° = 0$, entire xy plane is a node (zero probability of finding the p_y electron in xz plane). **65.**

$Y(\theta\phi)$

Positive phase

Negative phase

67.

$Y^2(\theta\phi)$

Positive phase

Negative phase

69. A plot of radial probability distribution vs r/a_o for a 1s orbital gives a curve with a maximum at 1.0 ($r = a_o$), hence the maximum probability of finding an electron in hydrogen atom is at 0.53 pm. **71. (a)** 3p **(b)** 3d **(c)** 4f **73.** $5d_{xy}$ **75.** Configuration (b) is correct, **(a)** violates the Pauli exclusion principle and **(c)** and **(d)** violate Hund's rule **77. (a)** 3; **(b)** 10; **(c)** 2; **(d)** 2; **(e)** 14 **79. (a)** three; **(b)** two; **(c)** zero; **(d)** fourteen; **(e)** two; **(f)** five (six with Z = 114); **(g)** thirty-two **81. (a)** Pb: $[Xe]4f^{14}5d^{10}6s^26p^2$; **(b)** 114: $[Rn]5f^{14}6d^{10}7s^27p^2$ **83.** Only (c) is a ground-state electron configuration (for nitrogen). **85. (a)** Au: $[Xe]4f^{14}5d^{10}6s^1$ **(b)** Mg: $[Ne]3s^2$ **(c)** Bi: $[Xe]4f^{14}5d^{10}6s^26p^3$ **(d)** In: $[Kr]4d^{10}5s^25p^1$ **(e)** Mo: $[Kr]4d^55s^1$

(f) Br: $[Ar]3d^{10}4s^24p^5$ **87. (a)** Ac **(b)** N **(c)** Ti **(d)** I **(e)** Ce

Integrative and Advanced Exercises
91. (a) The longest wavelength light for the photoelectric effect is 275 nm. This is UV light, not visible. **(b)** 2.02×10^{-19} J **(c)** 6.66×10^5 m/s **92.** 1.0×10^{20} photons/s **93.** $\lambda = 525$ nm, green **96.** From $n = 4$ to $n = 3$ **101.** 4.8 mJ **102.** 7×10^2 photon/s **105. (a)** 7.29×10^5 m/s **(b)** 2.43×10^{14} s^{-1}
Feature Problems 114. A plot of frequency versus n^{-2} gives a straight line plot with a slope $(-3.291 \times 10^{15}$ Hz) and y-intercept $(8.224 \times 10^{14}$ Hz), virtually identical to that predicted by the Balmer equation. **116.**
(a) Two lines would be observed in the absorption spectrum ($n = 1 \longrightarrow n = 2$ at 121.5 nm and $n = 1 \longrightarrow n = 3$ at 102.6 nm) **(b)** Six emission lines should be seen for the transitions $n = 4$ to $n = 3$ (1875 nm), $n = 4$ to $n = 2$ (486.1 nm), $n = 4$ to $n = 1$ (97.2 nm); from $n = 3$ to $n = 2$ (656.3 nm), $n = 3$ to $n = 1$ (102.5 nm); and from $n = 2$ to $n = 1$ (121.5 nm). **(c)** Two lines are common to the absorption and emission spectra.

CHAPTER 9
Practice Examples 1A. S **1B.** Ca
2A. $V^{3+} < Ti^{2+} < Ca^{2+} < Sr^{2+} < Br^-$ **2B.** As
3A. K $<$ Mg $<$ S $<$ Cl **3B.** Sb **4A.** Cl and Al are paramagnetic; the others are diamagnetic.
4B. Cr^{2+} **5A.** 280 K **5B.** 570 K
Exercises 1. 14 to 16 g/cm^3 **3.** Plot of density vs. atomic number has similar shape for both periods. **5.** Moseley discovered the link between atomic number and the periodic table. Thus, when all the elements with integral values in a certain range have been discovered, no new elements are possible in that range. **7. (a)** 118 **(b)** 119 **(c)** about 295 u and 298 u, respectively **9. (a)** Te **(b)** K **(c)** Cs **(d)** N **(e)** P **(f)** Au **11.** Electrons are being added to the same subshell in some instances but to a new subshell in others. **13. (a)** B **(b)** Te **15.** Li$^+$ $<$ Br $<$ Se $<$ I$^-$ **17.** Fe^{2+} and Co^{3+}; Sc^{3+} and Ca^{2+}; F$^-$ and Al^{3+}; Zn^{2+} and Cu$^+$ **19.** Yes, for example Cu$^+$ and Zn^{2+} **21.** Cs $<$ Sr $<$ As $<$ S $<$ F **23.** An electron may be attracted into a neutral atom in some cases and repelled in others, making EA a negative quantity in some cases and positive in others. The ejection of an electron from a neutral atom always requires an absorption of energy; I is always positive. **25.** 9952 kJ **27.** −456 kJ, exothermic **29.** The electron being removed from Na$^+$ must be removed from a positive ion, requiring a greater energy absorption than the removal of an electron from the neutral Ne atom. **31.** Only Fe^{2+}; the other ions all have noble-gas electron configurations. **33.** Diamagnetic: (a), (c), (d), (f); paramagnetic: (b), (e), (g) **35.** All atoms with odd Z must be paramagnetic, but some with even Z are also paramagnetic, for example, C. **37. (a)** Metals that should exhibit the photoelectric effect: Cs, Rb, and K (small first ionization energy); Zn, Cd, Hg should not (relatively large first ionization energies) **(b)** Rn **(c)** +600 kJ/mol **(d)** 5.7 g/cm^3 **39. (a)** 5.4 g/cm^3 **(b)** Ga$_2$O$_3$, 74% Ga **41.** 210 K **43. (a)** 1 **(b)** 1 **(c)** 3 **(d)** 4 **(e)** 2 **(f)** 2

Integrative and Advanced Exercises 47. Use data from Figure 9-8 and estimate the few missing data. Look for a group of four species in which two are of nearly equal radii, a third of twice the radius of the first two, and a fourth that is slightly larger than the third; **(b)** and **(e)** are best choices. **50.** Data yield an atomic mass of 75.7 u, indicating Gruppe V or Gruppe VI. **52.** Al: atomic radius about the same or larger, I_1 about the same or smaller; In: atomic radius larger, I_1 smaller; Se: atomic radius smaller, I_1 larger **54.** BrCl: mp $\approx$ 226 K, bp $\approx$ 286 K; ICl: mp $\approx$ 280 K, bp $\approx$ 348 K **57.** Yes, the data yield an atomic mass of 230 u, within about 4% of Mendeleev's assigned value. **60.** Value obtained, 5249 kJ/mol, in excellent agreement with the given 5251 kJ/mol **61.** Predicted: I_2 for Ba $< I_1$ for F $< I_3$ for Sc $< I_2$ for Na $< I_3$ for Mg [actual values: 965, 1681, 2389, 4562, and 7733 kJ/mol, respectively].
Feature Problems 66. A plot of $\nu^{1/2}$ versus Z provides $A = 2.30 \times 10^{15}$ Hz and $b = 0.969$.
67. (a) For [Ne]$3p^1$, $I_1 = 293$ kJ/mol; for [Ne]$4s^1$, $I_1 = 188$ kJ/mol; for [Ne]$3d^1$, $I_1 = 147$ kJ/mol; for [Ne]$4p^1$, $I_1 = 134$ kJ/mol. **(b)** For [Ne]$3p^1$, $Z_{eff} = 1.42$, for [Ne]$4s^1$, $Z_{eff} = 1.51$, for [Ne]$4p^1$, $Z_{eff} = 1.28$, for [Ne]$3d^1$, $Z_{eff} = 1.00$ **(c)** For [Ne]$3p^1$, $\bar{r}_{3p} = 4.7 \times 10^2$ pm, for [Ne]$4s^1$, $\bar{r}_{4s} = 8.4 \times 10^2$ pm, for [Ne]$4p^1$, $\bar{r}_{4p} = 9.5 \times 10^2$ pm, for [Ne]$3d^1$, $\bar{r}_{3d} = 5.6 \times 10^2$ pm. **(d)** The more deeply the orbital penetrates, the greater is its Z_{eff} and hence, the closer it is to the nucleus on average.

CHAPTER 10
Practice Examples

1A. ·Mg· ·Ge· K· :Ne:

1B. ·Sn· [:Br:]$^-$ [·Tl·]$^+$ [:S:]$^{2-}$

2A. (a) [Na]$^+$ [:S:]$^{2-}$ [Na]$^+$

(b) [Mg]$^{2+}$[:N:]$^{3-}$[Mg]$^{2+}$[:N:]$^{3-}$[Mg]$^{2+}$

2B. (a) [:I:]$^-$[Ca]$^{2+}$[:I:]$^-$

(b) [Ba]$^{2+}$[:S:]$^{2-}$

(c) [Li]$^+$[:O:]$^{2-}$[Li]$^+$

3A.

3B.

4A. P—Cl and N—H **4B.** P—O **5A.** The map with the most extensive red region is HF, signifying a high negative charge density associated with the high EN of F. **5B.** As in 5A, the most extensive red region is associated with an atom of high EN; in this case that is the O atom in CH$_3$OH.

6A. (a) S̈=C=S̈

(b) H—C≡N:

(c) :Cl̈—C—Cl̈:   (with :O: double bonded to C above)

6B. (a) H—C—Ö—H   (with :O: double bonded to C above)

(b) H—C—C—H   (with H's and :O: as shown)

7A. (a) [:N≡O:]$^+$

(b) [H—N—N:]$^+$ (with H's on N atoms)

(c) [:O:]$^{2-}$

7B. (a) [:F—B—F:]$^-$ (with :F: above and below B)

(b) [H—N—Ö—H]$^+$ (with H's on N)

(c) [:N≡C—Ö:]$^-$ or [:N̈=C=Ö:]$^-$

8A. :N̈=Ö—Cl̈: (with ⊖ under N and ⊕ under O)

Structure is less plausible because it has a positive formal charge on oxygen, the most electronegative atom in the molecule.

8B. H—N̈—C≡N: H—N̈=C=N̈: (with H's on N, ⊕ and ⊖ charges as shown)

The structure with no formal charges is the more plausible.

9A. :Ö—S̈=Ö: ⟷ :Ö=S̈—Ö: (with charges ⊖, ⊕, ⊖ as shown)

9B.

:Ö—N—Ö: ⟷ :Ö=N—Ö: (with :O: and charges as shown)

⟷ :Ö—N=Ö: (with :O: and charges as shown)

10A. trigonal-pyramidal **10B.** tetrahedral
11A. linear **11B.** linear
12A.

The H—C—H and H—C—O bond angles are $\sim$109.5°; C—O—H bond angle is slightly less than 109.5°.

12B.

The H—C—N, H—C—H and H—C—C angles are $\sim$109.5°. C—O—H bond angle is slightly less than 109.5° The O—C—O and O—C—C bond angles are $\sim$120°.
13A. H$_2$O$_2$: the individual bond moments do not cancel out. **13B.** PCl$_5$: the individual bond