Key to homework 7

8-2 Resonance fluorescence is a type of fluorescence in which the emitted radiation has a wavelength that is identical to the wavelength of the radiation used to excite the fluorescence.

8-4 Natural line widths in atomic spectroscopy are the widths of lines when only the uncertainty principle, and not Doppler and pressure broadening, contribute to the broadening. The widths are typically 10^{-5}nm (10^{-4}A). (Page 220, after Example8-1)

8-5 In the presence of KCl ionization of sodium is avoided because of the high concentration of electrons of ionization of potassium. In the absence of KCl some of the sodium is ionized, which leads to a lower intensity of the emission line for the atomic sodium.

8-6 The energy necessary to promote a ground state *s* electron to the next *p* level is so high for Cs that only a fraction of Cs atoms are excited at the temperature of a natural gas flame. At the higher temperature of a hydrogen/oxygen flame a much larger fraction of the atoms is excited and thus emit a more intense Cs line.

8-8 (a) $m = \dfrac{7.0\times10^{-3}\,kgNa/mol}{6.02\times10^{23}\,particlesNa/mol} = 1.16\times10^{-26}\,kg$

$$\nu = \sqrt{8kT/\pi m} = \sqrt{\frac{8\times1.38\times10^{-23}\,kg\cdot m^2\cdot s^{-2}\cdot K^{-1}\times2100K}{\pi\times1.16\times10^{-26}\,kg}} = 2.52\times10^{3}\,m/s$$

$$\Delta\lambda = \frac{\nu\lambda}{c} = \frac{2.52\times10^{3}\,m/s\times6707.76\times10^{-10}\,m}{3.00\times10^{8}\,m/s} = \underline{\underline{5.7\times10^{-12}\,m}} = \underline{\underline{5.7\times10^{-3}\,nm}}$$

(b) Proceeding in the same way, we find at 3150K, $\Delta\lambda = \underline{\underline{7.0\times10^{-3}\,nm}}$

8-9 $\dfrac{N_j}{N_0} = \dfrac{g_j}{g_0}\exp\left(\dfrac{-E_j}{kT}\right)$ (Equation 8-1)

The energies of the 3p states can be obtained from the emission wavelengths shown in Figure 8-1. For sodium we will use an average wavelength of 5893A and for Mg^{+}, 2800A.

For Na, the energy of the excited state is

$$E_{j,Na} = \frac{hc}{\lambda} = \frac{6.62\times10^{-34}\,J\cdot s\times3.00\times10^{8}\,m\cdot s^{-1}}{5893\times10^{-10}\,m} = 3.37\times10^{-19}\,J$$

For Mg^{+}, the energy of the excited state is

$$E_{j,Mg^+} = \frac{hc}{\lambda} = \frac{6.62\times10^{-34}\,J\cdot s\times3.00\times10^{8}\,m\cdot s^{-1}}{2800\times10^{-10}\,m} = 7.09\times10^{-19}\,J$$

(a) Substituting into Equation 8-1,

For Na,

$$\frac{N_{j,Na}}{N_0} = \frac{g_j}{g_0}\exp\left(\frac{-E_j}{kT}\right) = 3\exp\left(\frac{-3.37\times10^{-19}\,J}{1.38\times10^{-23}\,kg\cdot m^2\cdot s^{-2}\cdot K^{-1}\times1800K}\right) = \underline{\underline{3.8\times10^{-6}}}$$

For Mg^+,

$$\frac{N_{j,Mg^+}}{N_0} = \frac{g_j}{g_0}\exp\left(\frac{-E_j}{kT}\right) = 3\exp\left(\frac{-7.09\times10^{-19}\,J}{1.38\times10^{-23}\,kg\cdot m^2\cdot s^{-2}\cdot K^{-1}\times1800K}\right) = \underline{\underline{1.2\times10^{-12}}}$$

Proceeding the same way, we obtain for Na and Mg^+ respectively,

(b) 7.6×10^{-4} and 8.0×10^{-8}

(c) 0.10 and 2.5×10^{-3}

9-1 (a) A releasing agent is a cation which preferentially reacts with a species that would otherwise react with the analyte to cause a chemical interference.

(b) Protective agents prevent interference by forming stable and volatile products with the analyte.

(c) An ionization suppressor provides a high concentration of electrons in the flame. These electrons suppress ionization of the analyte.

(d) Atomization is the process in which a sample is vaporized and decomposed to its atoms, usually by heat.

(e) Pressure broadening refers to the broadening of atomic line widths at higher concentrations of atoms in flame.

(f) A hollow cathode lamp has a tungsten anode and a cylindric-shaped cathode containing the element of interest. The element is sputtered from the cathode into the gas phas. This process excites some of the gaseous atoms, which then emit their characteristic radiation as they return to the ground state.

(g) Sputtering is the process in which gaseous cations bombard a cathode and eject atoms from the cathode into the gas phase.

(h) Self-absorption refers to the absorption of radiation by unexcited atoms in the gas phase of a hollow cathode lamp or other source.

(i) Spectral interference is encountered when the absorption or emission of a nonanalyte species overlaps a peak being used for the determination of the analyte.

(j) Chemical interference is the result of any chemical process which decreases or increases the absorption or emission characteristics of the analyte.

(k) A radiation buffer is an substance added in excess to both sample and standards, which swamps out the effect of the sample matrix on the analyte emission or aborption.

(l) Doppler broadening arises because atoms moving toward or away from the monochromator give rise to absorption or emission lines at slightly different frequencies.

9-5 Source modulation is employed to distinguish between the component of light arising from the source and the component of light arising form the flame background.

9-9 At high currents, more unexcited atoms are formed in the sputtering process. These atoms generally have less kinetic energy than the excited ones. The Doppler broadening of their absorption lines is therefore less than the broadening of the emission lines of the faster moving excited atoms. Thus, only the center of the emission line is attenuated by self-absorption.

9-14 Proceed as in question 8-9

10-2 Flame atomic absorption methods require a separate lamp for each element, which is not convenient when several elements are to be determined.

10-3 The temperature of a spark plasma is so great (~40000K) that most atoms present are ionized. In a lower temperature arc (~4000K) only the lighter elements are ionized to any significant extent. In a plasma, the high concentration of electrons prevents extensive ionization of the analyte atoms.

10-6 By nebulization, by electothermal vaporization, and by a high-voltage electric spark.

10-9 Advantages of plasma sources over flame sources include:

(1) Lower interelement interference.

(2) Emission spectra for most elements can be obtained with a single set of excitation conditions.

(3) Spectra can be obtained for low concentrations of elements that tend to form refractory compounds.

(4) Plasma sources usually have concentration ranges that cover several decades.