Homework 8 Solutions

8-1 The flame absorption peak for calcium in a low-temperature flame is broad because the calcium is largely present as the calcium molecule CaOH, which has many vibrational and rotational states and thus many excited energy levels. Thus a broad molecular absorption peak is observed. In contrast, barium is apparently present only as atoms that only absorb at a few discrete wavelengths.

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.

8-5 In the presence of KCl ionization of sodium is avoided because of the high concentration of electrons from 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 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 small fraction of the Cs atoms are excited at the temperature of the natural gas flame. At the higher temperature of the hydrogen/oxygen flame a much larger fraction of the atoms is excited and thus a more intense emission line for Cs is observed.

8-9 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 5893 Å and for Mg*, 2800 Å.

For Na, the energy of the excited state is

\[ E_{y_1} = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}^2}{5893 \text{ Å} \times 10^{-10} \text{ m Å}} = 3.37 \times 10^{-19} \text{ J} \]

For Mg*

\[ E_{y_2} = \frac{6.62 \times 10^{-34} \times 3.00 \times 10^8}{2800 \times 10^{-10}} = 7.09 \times 10^{-19} \text{ J} \]

(a) Substituting into Equation 8-1 (page 199) gives for 2100 K,

\[ N_{y_1}/N_0 = 3 \exp \left( -\frac{3.37 \times 10^{-19} \text{ J}}{1.38 \times 10^{23} \text{ JK}^{-1} \times 2100 \text{ K}} \right) = 2.7 \times 10^{-5} \]

\[ N_{y_2}/N_0 = 3 \exp \left( -\frac{7.09 \times 10^{-19} \text{ J}}{1.38 \times 10^{23} \times 2100} \right) = 7.1 \times 10^{-11} \]

Proceeding in the same way, we obtain for Na and Mg* respectively,

(b) \( N_{y_1}/N_0 = 6.6 \times 10^{-4} \) and \( 6.1 \times 10^{-4} \)

(c) \( N_{y_2}/N_0 = 5.1 \times 10^{-2} \) and \( 5.7 \times 10^{-4} \)
8-10. The key to solving this is simply in seeing the ordering of the energy levels. \(3s \to 3p \to 4s\) – the energy level diagram for Na Figure 8-1 is essential. The energy difference between the 3p and 3s state for sodium was \(3.37 \times 10^{-19}\) J. The energy difference between the 4s and 3p state can be calculated from the emission wavelength, 1139 nm. The energy difference from 4s to 3s is simply the sum of these two steps.

\[
E_{4s}^\gamma = \frac{6.62 \times 10^{-34} \text{J s} \times 3.00 \times 10^8 \text{m s}^{-1}}{1139 \text{ nm} \times 10^{-9} \text{nm/m}\text{m}} = 1.74 \times 10^{-19} \text{J}
\]

The energy difference between the 4s and 3s state is

\[
E_{4s}^\gamma = 3.37 \times 10^{-19} + 1.74 \times 10^{-19} = 5.11 \times 10^{-19} \text{J}
\]

Applying Equation 8-1 gives

(a) At 3000°C = 3273 K

\[
\frac{N_{4s}}{N_{3s}} = \frac{2}{2} \exp \left( -\frac{5.11 \times 10^{-19}}{1.38 \times 10^{-23} \text{JK}^{-1} \times 3272} \right) = 1.2 \times 10^{-5}
\]

(b) At 9000°C = 9273 K

\[
\frac{N_{4s}}{N_{3s}} = \exp \left( -\frac{5.11 \times 10^{-19}}{1.38 \times 10^{-23} \times 9273} \right) = 1.8 \times 10^{-2}
\]

8-11 This behavior would result from ionization of the U. At low concentrations, the fraction of U that is ionized would be greater thus giving a nonlinear relationship between concentration and absorbance.

8-11. This was a tricky one – but not that complex once you understand the dynamic. The low absorbance at low concentration implies the loss of U-atoms at low concentration. One loss mechanism is ionization. Ionization, just like for a weak acid for example, is more extensive at low concentration because of the equilibrium expression:

\[
K_{\text{ION}} = \frac{[U^{\text{iii}}][e^-]}{[U]}
\]

Total U atom species entering the plasma \(= [U_0]\)

U atoms left after ionization \(= [U] = [U_0] - x\) (this is what we want)

U ions formed \(= [x]\)

Electrons released \(= [e^-] = [x]\)

\[
K_{\text{ION}} = \frac{x^2}{[U_0] - x}
\]

Now drop the ‘ion’ subscript and the parentheses

\[
KU_0 - Kx = x^2
\]

\[
x^2 + Kx - KU_0 = 0 \Rightarrow \text{Quadratic...} a = 1, b = K, c = -KU_0
\]

\[
x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}
\]

\[
x = \frac{-K \pm (K^2 + 4KU_0)^{1/2}}{2}
\]

\[
\Rightarrow [U] = [U_0] - x = \text{nonlinear at low [U_0] concentrations... see graphs on following page:}
\]
Assumed ionization constant: \( K = 10^{-4} \)

Concentration of ions: 
\[
x(K, U_0) = \frac{-K + \sqrt{K^2 + 4KU_0}}{2}
\]

Fraction ionized:

\[
x(K, U_0) \frac{U_0}{U_0^2}
\]