

CHEM 221
Instrumental Analysis
Problem Set #4 – Solutions
Spring 2005

Chapter 8

- #5.** Emission from Na *atoms* increases in a hot flame upon addition of KCl due to a shift in the Na ionization equilibrium:



Adding an easily ionizable element (e.g., K) increases the electron density, shifting the above equilibrium to the **left**, increasing the Na atom density and, thus, the Na atom emission intensity increases.

8-8 (a) $v = \sqrt{8kT/\pi m}$

From the table of energy conversion factors (inside the front cover of the text), the Boltzmann constant k is equal to

$$k = 1.38 \times 10^{-23} \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1}$$

Thus

$$\begin{aligned} v &= \sqrt{\frac{8 \times 1.38 \times 10^{-23} \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \times 2200 \text{ K}}{\pi \times 23.0 \times 10^{-3} (\text{kg Na/mol}) / (6.02 \times 10^{23} \text{ particles Na/mol})}} \\ &= 1.42 \times 10^3 \text{ m/s} \end{aligned}$$

$$\begin{aligned} \Delta\lambda &= \frac{v\lambda}{c} = \frac{1.42 \times 10^3 \text{ m} \cdot \text{s}^{-1} \times 5893 \text{ \AA} \times 10^{-10} \text{ m/\AA}}{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}} \\ &= 2.79 \times 10^{-12} \text{ m} \text{ or } \underline{\underline{0.028 \text{ \AA}}} \end{aligned}$$

- (b) Proceeding in the same way, we find at 3000 K, $\Delta\lambda = \underline{\underline{0.033 \text{ \AA}}}$

Chapter 9

- #3.** Graphite furnaces make more efficient use of sample and provide a much longer sample residence time in the optical beam (as compared with a flame).
- #9.** For atomic absorption and fluorescence, signal is proportional to the *ground state* atom population (which is relatively invariant with changing temperature). The atomic emission signal is proportional to the *excited state* atom population which, according to Boltzmann, is very sensitive to changes in temperature.
- #19.** Analyte emission intensities are sensitive to even small changes in flame temperature (recall the answer to Question #9), but by using the *ratio* of emission intensities of the analyte and an *internal standard* (added at a fixed concentration in all standards and unknowns), any temperature- or sample aspiration rate-induced emission fluctuations will be compensated for.

Chapter 10

- #2.** Flame AAS requires a separate lamp for *each element*, making multielement determinations very time-consuming. ICP-AES has no such limitation.
- #8.** Ionization interferences are less severe in ICPs than in flames due to the buffering effect of the naturally high electron concentration in ICPs.

Chapter 15

- #2.** A fluorescence emission spectrum is obtained by using a fixed excitation wavelength and scanning the emission monochromator. A fluorescence excitation spectrum is obtained by monitoring emission at a fixed wavelength while scanning the excitation monochromator. The excitation spectrum should most closely resemble the absorption spectrum as it essentially is using the emission process as an indicator of the degree of absorption that occurs at different wavelengths illuminating the sample.
- #3.** In spectrofluorometry, detection is ultimately limited by the ability to distinguish between two very small signals (the blank and the emission from a very low concentration sample). In

spectrophotometry (absorption), detection is limited by the ability to distinguish between two very LARGE signals (I_0 and the transmitted signal through a very weakly absorbing sample). Since shot noise is related to the magnitude of the signal, the ability to differentiate between two LARGE signals is considerably less than the ability to differentiate between two SMALL signals. Thus, spectrofluorometric detection limits are lower than corresponding spectrophotometric detection limits.

#4. Fluorescence quantum efficiency is enhanced by rigidity in the molecular structure of a molecule. Phenolphthalein's three rings are tethered to a central carbon atom and two have the freedom to rotate about the bond axis; this is not a rigid framework. Fluorescein, however, has three FUSED RINGS, giving it a rigid structure, so it will have a higher fluorescence quantum yield.

Chapter 18

#3. a. The Rayleigh scatter line is at the excitation wavelength:

$$632.8 \text{ nm} = 6328 \text{ \AA} = 6328 \times 10^{-8} \text{ cm} \rightarrow 15,802.78 \text{ cm}^{-1}$$

Anti-Stokes lines will be at *greater* energy, so for the 218 cm^{-1} line:

$$15,802.78 \text{ cm}^{-1} + 218 \text{ cm}^{-1} = 16,020.78 \text{ cm}^{-1}$$

Converting back to nanometers:

$$16,020.78 \text{ cm}^{-1} \rightarrow 6242 \times 10^{-8} \text{ cm} = 6242 \text{ \AA} = \mathbf{624.2 \text{ nm}}$$

For the Stokes lines, we *subtract* the Raman shift from the Rayleigh line (lower energy).

Using this method, we obtain:

<u>Raman Line</u>	<u>AntiStokes</u>	<u>Stokes</u>
218 cm^{-1}	624.2 nm	641.7 nm
314	620.5	645.6
459	614.9	651.7
762	603.7	664.9
790	602.7	666.1

b. For the argon-ion laser, we repeat the same calculations, except we use a Rayleigh scatter wavelength of 488.0 nm (= 20,491.80

cm⁻¹). Adding and subtracting the Raman lines to this to get the Stokes and Anti-Stokes wavelengths:

<u>Raman Line</u>	<u>AntiStokes</u>	<u>Stokes</u>
218 cm ⁻¹	482.9 nm	493.2 nm
314	480.6	495.6
459	477.3	499.2
762	470.5	506.8
790	469.9	507.6

- #4. a.** Raman scatter intensities are proportional to $1/\lambda^4$. Changing lasers, results in a factor of $632.8/488.0 = 1.2967$ wavelength change. So:

$$(1.2967)^4 = \mathbf{2.83}$$

So, the Raman spectrum acquired using the argon-ion laser (at 488.0 nm) will be **2.83** times more intense than the spectrum obtained with the 632.8 nm HeNe laser line.

b. The actual intensity ratio that would be observed would depend upon the relative response functions of the PMT/Monochromator system used at those two wavelengths (the PMT quantum efficiency varies with wavelength as does the transmittance properties of the monochromator).

- #5.** Fluorescence is typically excited at shorter wavelengths (corresponding to higher energy transitions), so the longer wavelength afforded by the HeNe laser would be less likely to produce a fluorescence background that could obscure the weaker Raman scattered radiation.