CHEMISTRY 133
HW 2.1 Solutions
Text Problems

Ch. 17: 3, 4, 11, 16, 24

3. Calculate the frequency (in hertz), wavenumber (in cm^{-1}), and energy (in joules per photon and joules per mole of photons) of visible light with a wavelength of 562 nm.

frequency: $\mu = c/\lambda = 3.00 \times 10^8$ m s^{-1}/(562 nm*1x10^{-9} m/nm) = **5.33×10^{14} Hz**.

wavenumber: $\tilde{\nu} = 1/\lambda = 1/(5.62 \times 10^{-5}$ cm) = **1.78×10^4 cm^{-1}**

Energy: $E = hc/\lambda = 6.63 \times 10^{-34}$J*s*3.00 x 10^8 m s^{-1}/(562 nm*1x10^{-9} m/nm) = **3.54×10^{-19} J**

$E = N*E_{photon} = 6.02 \times 10^{23}*3.54 \times 10^{-19}$ J = **2.13×10^5 J/mole.**

4. Which molecular processes correspond to the enrgies of microwave, infrared, visible and ultraviolet photons:

Type of Light	Microwave	Infrared	Visible	Ultraviolet
Process	*Rotation*	*Vibration*	*Electronic states (e.g. for molecules in eye)*	*Electronic states*

11. The absorbance of a 2.31×10^{-5} M solution of a compound is 0.822 at a wavelength of 266 nm in a 1.00 cm cell. Calculate the molar absorptivity at 266 nm.

$A = 0.822 = \varepsilon bC = \varepsilon*1.00$ cm*2.31 x 10^{-5} M

ε = 0.822/1.00 cm*2.31 x 10^{-5} M = **3.56×10^4 M^{-1} cm^{-1}**.

16. A compound with a molecular mass of 292.16 was dissolved in a 5 mL volumetric flask. A 1.00 mL aliquot was withdrawn, placed in a 10 mL volumetric flask, and diluted to the mark. The absorbance at 340 nm was 0.427 in a 1.00 cm cuvet. The molar absorptivity for this compound at 340 nm is 6130 M^{-1} cm^{-1}.

a) Calculate the concentration of the compound in the cuvet.

$C = A/\varepsilon b = 0.427/[(6130\ M^{-1}\ cm^{-1})(1\ cm)]$ = **6.97×10^{-5} M**

b) What was the concentration of compound in the 5 mL flask?

$C_{conc}V_{conc} = C_{dil}V_{dil}$ so $C_{conc} = (6.97 \times 10^{-5}$ M)10/1 = **6.97×10^{-4} M**

c) How many milligrams of compound were used to make the 5 mL solution?

Mass = (6.97×10^{-4} mmol/mL)(5 mL)(292.16 mg/mmol) = **1.02 mg**

24. What is the difference between fluorescence and phosphorescence?

Fluorescence is the emission of light as a molecule (or atom) returns from an excited electronic state to the ground state. The excited state will have the opposite spin as the highest occupied molecular orbital (homo) electron. Phosphorescence consists of the same process with the exception of the excited state having the same spin as the homo electron. As a result, phosphorescence is less likely to occur.

Ch. 19: 1, 3-6, 10, 11, 13, 28

1. Describe the role of each component of the spectrophotometer in Figure 19-1.
The light source provides light for absorption by the sample, the scanning monochromator selects one wavelength to pass through the samples, the beam chopper splits the beam between reference and sample cell paths, the sample contains the analyte absorbing light and a reference solution contains the same solvent as the sample solution, the detector converts the photons into an electrical response, an amplifier increases the response and the display displays the data.

3. Would you use a tungsten or a deuterium lamp as a source of 300 nm radiation?
A deuterium lamp (better for UV light).
What kind of lamp provides radiation at 4-μm wavelength?
4-μm is in the infrared range (corresponds to a wavenumber of 2500 cm^{-1}). The globar would be a good light source.

4. Which variables increase the resolution of a grating? *The number of lines illuminated (the more illuminated the higher the resolution) and the order of light originating from the grating.*
Which variables increase the dispersion of the grating?
Increases in the order of the dispersed light, the number of grating lines per centimeter and the angle from normal for light leaving the grating all increase the dispersion of the grating.
How is the blaze angle chosen to optimize a grating for a particular wavelength?
A blaze angle is chose so that the incoming and outgoing angles with respect to the facet normal are nearly equal at an exit angle that gives the desired wavelength.

5. What is the role of a filter in a grating monochromator?
The filter is used to eliminate all but one order of light emitted from the diffraction grating. Normally, some higher order wavelengths can interfere with the desired wavelengths.

6. What are the advantages and disadvantages of decreasing monochromator slit width?
The advantage is higher resolution (better instrument selectivity and smaller Beer's law deviations). The disadvantage is less light through (this would, for example, decrease sensitivity in a fluorescent spectrometer).

10. Show that a grating with 10^3 grooves/cm provides a dispersion of 5.8° per μm of wavelength if n = 1 and φ = 10° in Equation 20-4.
$d = 1/(1000 \text{ grooves/cm}) = 0.001 \text{ cm} = 0.01 \text{ mm} = 10\ \mu m$
$\Delta\varphi/\Delta\lambda = n/d\cos\varphi = 1/[(10\ \mu m)\cos(10°)]$
$= 1/(10\cdot 0.985\ \mu m) = (0.102 \text{ radians}/\mu m)\cdot(180 \text{ degrees}/\pi \text{ radians}) = \mathbf{5.8\ °/\mu m}$

11. a) What resolution is required for a diffraction grating to resolve wavelengths of 512.23 and 512.26 nm?
$\Delta\lambda = 512.26 \text{ nm} - 512.23 \text{ nm} = 0.03 \text{ nm}$
$\text{Resolution} = \lambda/\Delta\lambda = 512/0.03 = \mathbf{17{,}000}$
b) With a resolution of 10^4, how close in nm is the closest line to 512.23 nm that can barely be resolved?
$\text{Resolution} = \lambda/\Delta\lambda = 10{,}000$

$\Delta\lambda$ =512.23/10,000 = ***0.05 nm***
c) Calculate the fourth-order resolution of a grating that is 8.00 cm long and is ruled at 185 lines/mm.
resolution = nN = 4(80 mm)(185 lines/mm) = ***5.9×10^4***.
d) Find the angular dispersion ($\Delta\varphi$) between light rays with wavelengths of 512.23 and 512.26 nm for first-order diffraction (n = 1) and thirtieth-order diffraction from a grating with 250 lines/mm and φ = 3.0°.
$\Delta\lambda$ = 0.03 nm, d = 1/250 = 0.004 mm
$\Delta\varphi/\Delta\lambda = n/d\cos\varphi$
n = 1: $\Delta\varphi = n\Delta\lambda/d\cos\varphi$ = (0.03 nm)/[0.004 mm·cos(3)] = 7.5×10^{-6} radians = ***0.0004°***
n = 30: $\Delta\varphi = n\Delta\lambda/d\cos\varphi$ = 30(7.5×10^{-6} radians) = 2.25×10^{-4} radians = ***0.013°***

13. The pathlength of a cell for infrared spectroscopy can be measured by counting interference fringes (ripples in the transmission spectrum). The spectrum below shows 30 interference maxima between 1906 and 698 cm obtained by placing an empty KBr cell in a spectrometer. ... Calculate the pathlength of the cell that gave the interference fringes shown earlier.
*$b = (N/2n)[1/(\bar{\upsilon}_1 - \bar{\upsilon}_2)]$ = (30/2*1.0003)[1/(1906 – 698 cm^{-1})] =* ***0.124 mm***

28. The interferometer mirror of a Fourier transform infrared spectrophotometer travels ± 1 cm.
a) How many centimeters is the maximum retardation, Δ?
±2 cm
b) State what is meant by resolution.
Resolution refers to the ability to separate neighboring peaks
c) What is the approximate resolution (cm^{-1}) of the instrument?
$1/\Delta$ = ***0.5 cm^{-1}***
d) At what retardation interval, δ, must the interferogram be sampled (converted into digital form) to cover a spectral range of 0 to 2000 cm^{-1}?
$\delta = 1/(2\Delta\nu) = 1/(4000\ cm^{-1})$ = **2.5 μm**