PROBLEMS

2.1 A molecule absorbs radiation of frequency 3.00×10^{14} Hz. What is the energy difference between the molecular energy states involved?

2.2 What frequency of radiation has a wavelength of 500.0 nm?

2.3 Describe the transition that occurs when an atom absorbs UV radiation.

2.4 Arrange the following types of radiation in order of increasing wavelength: IR, radiowaves, X-rays, UV, and visible light.

2.5 For a given transition, does the degree of absorption by a population of atoms or molecules depend on the number in the ground state or the excited state? Explain.

2.6 For a given transition, does the intensity of emission by a population of atoms or molecules depend on the number in the ground state or the excited state? Explain.

2.7 Briefly describe three types of transitions that occur in most molecules, including the type of radiation involved in the transition.

2.8 State the mathematical formulation of the Beer–Lambert–Bouguer Law and explain the meaning of each symbol in the equation.

2.9 (a) Define transmittance and absorbance.
(b) What is the relationship between concentration and (1) transmittance, (2) absorbance?

2.10 Using Fig. 2.16, calculate the slope of the tangent drawn through the lower point marked B by extending the line to cover a 10-fold difference in concentration. Confirm that the range shown for B–B for 1% R.E. is correct by finding where on the upper portion of the curve you have a slope equal to the one you just calculated. Repeat the calculation for point C and confirm the C–C range.

2.11 The following data were obtained in a external standard calibration for the determination of iron by measuring the transmittance, at 510 nm and

1.00 cm optical path, of solutions of Fe^{2+} reacted with 1, 10-phenanthroline to give a red-colored complex.

Fe conc. (ppm)	%T	Fe conc. (ppm)	%T
0.20	90.0	3.00	26.3
0.40	82.5	4.00	17.0
0.60	76.0	5.00	10.9
0.80	69.5	6.00	7.0
2.00	41.0	7.00	4.5

(a) Calculate A, the absorbance, for each solution and plot A against concentration of iron. (You can do this using a spreadsheet program very easily.) Does the system conform to Beer's Law over the entire concentration range? (b) Calculate the average molar absorptivity of iron when it is determined by this method. (c) Plot $(100 - \%T)$ against log concentration (Ringbom method). (1) What are the optimum concentration range and the maximum accuracy (percent relative error per 1% transmittance error) in this range? (2) Over what concentration range will the relative analysis error per 1% transmittance error not exceed 5%?

2.12 The following data were obtained in a standard calibration for the determination of copper, as $Cu(NH_3)_4^{2+}$, by measuring the transmittance using a filter photometer.

Cu conc. (ppm)	%T	Cu conc. (ppm)	%T
0.020	96.0	0.800	27.8
0.050	90.6	1.00	23.2
0.080	84.7	1.40	17.2
0.100	81.4	2.00	12.9
0.200	66.7	3.00	9.7
0.400	47.3	4.00	8.1
0.600	35.8		

Calculate A, the absorbance, for each solution and plot A against concentration of copper. (You can do this using a spreadsheet program very easily.) Does the system, measured under these conditions, conform to Beer's Law over the entire concentration range? Is any deviation from the law of small or of large magnitude? Suggest a plausible cause for any deviation.

2.13 An amount of 0.200 g of copper is dissolved in nitric acid. Excess ammonia is added to form $Cu(NH_3)_4^{2+}$, and the solution is made up to 1 L. The following aliquots of the solution are taken and diluted to 10.0 mL: 10.0, 8.0, 5.0, 4.0, 3.0, 2.0, and 1.0 mL. The absorbances of the diluted solution were 0.500, 0.400, 0.250, 0.200, 0.150, 0.100, and 0.050, respectively. A series of samples was analyzed for copper concentration by forming the $Cu(NH_3)_4^{2+}$ complex and measuring the absorbance. The absorbances were (a) 0.450, (b) 0.300, and (c) 0.200. What were the respective concentrations in the three copper solutions? If these three samples were obtained by weighing out separately (a) 1.000 g, (b) 2.000 g, and (c) 3.000 g of sample, dissolving and diluting to 10.0 mL, what was the original concentration of copper in each sample?

2.14 Describe the standard addition method for measuring concentration of an unknown. What are the advantages of this method of calibration?

2.15 Describe the use of an internal standard for calibration. What characteristics must a species possess to serve as an internal standard? What are the advantages of the internal standard method?

2.16 Describe what you would do for samples whose absorbances fell above the absorbance of your highest calibration standard.

2.17 What range of % transmittance results in the smallest relative error for an instrument limited by (a) noise in the thermal detector of an IR spectrometer? (b) shot-noise?

2.18 What is A if the percentage of light absorbed is (a) 90%, (b) 99%, (c) 99.9%, and (d) 99.99%.

2.19 What is the purpose of having and measuring a reagent blank?

2.20 An optical cell containing a solution was placed in a beam of light. The original intensity of the light was 100 units. After being passed through the solution, its intensity was 80 units. A second similar cell containing more of the same solution was also placed in the light beam behind the first cell. Calculate the intensity of radiation emerging from the second cell.

2.21 The transmittance of a solution 1.00 cm thick of unknown concentration is 0.700. The transmittance of a standard solution of the same material is also 0.700. The concentration of the standard solution is 100.0 ppm; the cell length of the standard is 4.00 cm. What is the concentration of the unknown solution?

2.22 A solution contains 1.0 mg of $KMnO_4$/L. When measured in a 1.00 cm cell at 525 nm, the transmittance was 0.300. When measured under similar conditions at 500 nm, the transmittance was 0.350. (a) Calculate the absorbance A at each wavelength. (b) Calculate the molar absorptivity at each wavelength. (c) What would T be if the cell length were in each case 2.00 cm? (d) Calculate the absorptivity (if concentration is in mg/L) for the solution at each wavelength.

2.23 A series of standard ammoniacal copper solutions was prepared and the transmittance measured. The following data were obtained:

Cu concentration	Transmittance
0.20	0.900
0.40	0.825
0.60	0.760
0.80	0.695
1.00	0.635
2.00	0.410
3.00	0.263
4.00	0.170
5.00	0.109
6.00	0.070

Sample	Transmittance
1	0.840
2	0.470
3	0.710
4	0.130

Plot the concentration against absorbance (use your spreadsheet program). The transmittance of solutions of copper of unknown concentrations was also measured in the same way and the sample data in the above table were obtained. Calculate the concentration of each solution. What is missing from this experiment? List two things a good analytical chemist should have done to be certain that the results are accurate and precise.

2.24 List the components of a single-beam optical system for absorption spectroscopy. List the components of single-beam optical system for emission spectroscopy.

2.25 Describe the components in a grating monochromator. Briefly discuss the role of each component.

2.26 State the equation for the resolution of a grating.

2.27 (a) Define mechanical slit width.
(b) Define spectral bandpass or bandwidth.

2.28 What is the effect of mechanical slit width on resolution?

2.29 Write the expression for resolution of a grating ruled to be most efficient in second order. To resolve a given pair of wavelengths, will you need more or fewer lines if the grating were ruled in first order?

2.30 What resolution is required to separate two lines λ_1 and λ_2?

2.31 What resolution is required to resolve the Na D lines at 589.0 and 589.5 nm in first order?

2.32 How many lines must be illuminated on a grating to separate the Na D lines in second order?

2.34 A grating contains 1000 lines. Will it resolve two lines of λ 500.0 and 499.8 nm in first order if all 1000 lines are illuminated?

2.35 What are the components of a double-beam system? Describe two types of beam splitters.

2.36 How does a double-beam system correct for drift? Draw the alternating signal output from a double-beam system for a sample that absorbs 25% of the incident light.

2.37 Give an example of an absorption filter. Over what wavelength range do absorption filters function as wavelength selectors?

2.38 What are the advantages of absorption filters as wavelength selectors compared with gratings? What are the disadvantages?

2.39 Light of 300.0 nm is diffracted from a grating in first order at an angle of incidence normal to the grating (i.e., $i = 0°$). The grating contains 1180 grooves/mm. Calculate the angle of diffraction, θ, for this wavelength.

2.40 If an emission line for magnesium appears at 285.2 nm in first order, where will it appear in second order? Where will it appear in third order? If you needed to measure a first order iron emission line at 570 nm, will the presence of magnesium in the sample cause a problem? What can you do to solve the problem if one exists?

2.41 What are the major differences between an FT system and a dispersive system for spectroscopy?

2.42 Define the throughput advantage. How does it arise?

2.43 Define the multiplex advantage. How does it arise?

2.44 Draw two cosine waves of the same amplitude in phase. Draw the resulting wave if the two waves are combined. Draw two cosine waves 180° out of phase. Draw the resulting wave if these two waves are combined.

2.45 What is the difference between a spectrometer and a photometer? What is the difference between a spectrometer and a spectrograph?