AP Mini-Lesson

SPECTROSCOPY & SPECTROPHOTOMETERS

Spectroscopy is a general term referring to measurements & calculations based on colors of light. A *spectrophotometer* is a device that came be used to measure the concentration of colored solutions. It only works with colored solutions, because it is designed to measure the absorbance by the solution of particular wavelengths (colors) of the spectrum. A clear colorless solution is not absorbing any visible wavelengths, therefore a spectrophotometer cannot be used.

How does it work, exactly? A sample of colored solution is placed in a closed chamber and a beam of white light is directed through the solution. As you may know from other science courses, 'white' light is actually a mixture of all wavelengths (colors) of visible light. (The range of colors contained in white light is called the visible *spectrum*.) As this light beam passes through the solution, some of the wavelengths (colors) are absorbed more than others. The light emerging from the solution is analyzed by the spectrophotometer and the absorption of particular wavelengths of light can be determined.

Most colored substances absorb a range of different wavelengths. However, the spectrophotometer can only be set to one particular wavelength at a time. Typically there is one wavelength that is absorbed most strongly by a substance. This wavelength is usually the one chosen as the spectrophotometer setting.

See 2006 Form B question 5, part (a)

There is a simple relationship between the degree of absorbance and the concentration or molarity of the solution: they are directly proportional. In other words, the higher the molarity, the greater the absorbance. Quantities that are in direct proportion graph as a straight line. They can be described mathematically by a simple equation of the form

$$Y = k * X$$

Using A for absorbance and [X] for the concentration in molarity of the substance, the above equation becomes:

$$A = k * [X]$$

In spectroscopy, this is known as ***Beer's Law***. The k term would be a constant whose value would be the slope of the straight-line graph of absorbance vs. concentration. Sometimes Beer's Law is given in a more complex form, something like

$$A = a * b * [X]$$

In this equation, the *a* stands for an 'absorption constant' (different values for different solutions & wavelenths) and b would be the 'path length' of the sample—how far the beam of light travels through the solution. The combined value of *a* and *b* is equivalent to k in the first equation.

If you measure the absorbances of solutions with known concentrations, you can create a calibration graph for the spectrophotometer. In theory, the concentration of an unknown solution could then be determined by measuring its absorbance and seeing where it falls on the calibration graph.

See 2006 Form B question 5, part (b)

Once the molarity of a solution has been determined using spectroscopic information, the AP test may have some additional questions. These are questions based on chemical principles and calculations, and wouldn't really have anything more to do with the spectrophotometer.

See 2006 Form B question 5, part (c)

Sometimes you have to put together what you know about the spectrophotometric measurement and the calculations you will make based on them.

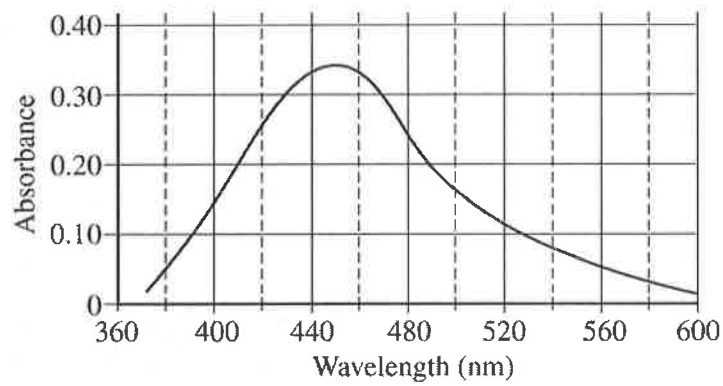
See 2006 Form B question 5, part (d)

For additional practice, see question #5 from 2003 and question #3 from 2004.

Question 5

5. A student carries out an experiment to determine the equilibrium constant for a reaction by colorimetric (spectrophotometric) analysis. The production of the red-colored species $FeSCN^{2+}(aq)$ is monitored.

(a) The optimum wavelength for the measurement of $[FeSCN^{2+}]$ must first be determined. The plot of absorbance, A, versus wavelength, λ, for $FeSCN^{2+}(aq)$ is given below. What is the optimum wavelength for this experiment? Justify your answer.



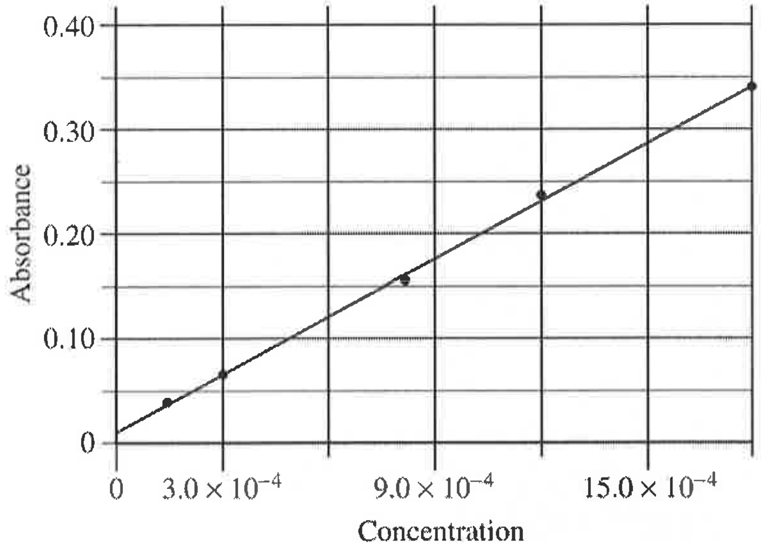
The optimum wavelength is 450 nm because that is the wavelength of maximum absorbance by $FeSCN^{2+}(aq)$.	One point is earned for the correct answer with justification.

(b) A calibration plot for the concentration of $FeSCN^{2+}(aq)$ is prepared at the optimum wavelength. The data below give the absorbances measured for a set of solutions of known concentration of $FeSCN^{2+}(aq)$.

Concentration ($mol\ L^{-1}$)	Absorbance
1.1×10^{-4}	0.030
3.0×10^{-4}	0.065
8.0×10^{-4}	0.160
12×10^{-4}	0.239
18×10^{-4}	0.340

Question 5 (continued)

(i) Draw a Beer's law calibration plot of all the data on the grid below. Indicate the scale on the horizontal axis by labeling it with appropriate values.



One point is earned for a straight-line plot. One point is earned for a correctly scaled horizontal axis.

(ii) An $FeSCN^{2+}(aq)$ solution of unknown concentration has an absorbance of 0.300. Use the plot you drew in part (i) to determine the concentration, in moles per liter, of this solution.

See plot in part (i). At $A = 0.300$, $[FeSCN^{2+}]$ is approximately 16×10^{-4} mol L^{-1}.	One point is earned for the correct answer.

Question 5 (continued)

(c) The purpose of the experiment is to determine the equilibrium constant for the reaction represented below.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$$

(i) Write the equilibrium-constant expression for K_c.

$K_c = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$	One point is earned for the correct expression.

(ii) The student combines solutions of $Fe(NO_3)_3$ and KSCN to produce a solution in which the initial concentrations of $Fe^{3+}(aq)$ and $SCN^{-}(aq)$ are both 6.0×10^{-3} *M*. The absorbance of this solution is measured, and the equilibrium $FeSCN^{2+}(aq)$ concentration is found to be 1.0×10^{-3} *M*. Determine the value of K_c.

	$Fe^{3+}(aq)$	+	$SCN^{-}(aq)$	$\rightleftarrows$	$FeSCN^{2+}(aq)$
I	6.0×10^{-3} *M*		6.0×10^{-3} *M*		0
C	-1.0×10^{-3} *M*		-1.0×10^{-3} *M*		$+1.0 \times 10^{-3}$ *M*
E	5.0×10^{-3} *M*		5.0×10^{-3} *M*		$+1.0 \times 10^{-3}$ *M*

$$K_c = \frac{1.0 \times 10^{-3}}{(5.0 \times 10^{-3})(5.0 \times 10^{-3})} = 40.$$

One point is earned for the correct equilibrium concentration.

One point is earned for the correct substitutions <u>and</u> the calculated value.

(d) If the student's equilibrium $FeSCN^{2+}(aq)$ solution of unknown concentration fades to a lighter color before the student measures its absorbance, will the calculated value of K_c be too high, too low, or unaffected? Justify your answer.

The value of K_c will be too low; the lower absorbance reading indicates a lower $[FeSCN^{2+}]$ than actually existed before the fading occurred, so substitution of a lower $[FeSCN^{2+}]$ into the equilibrium expression will result in a lower value of K_c.	One point is earned for the correct prediction. One point is earned for the correct justification.

2003

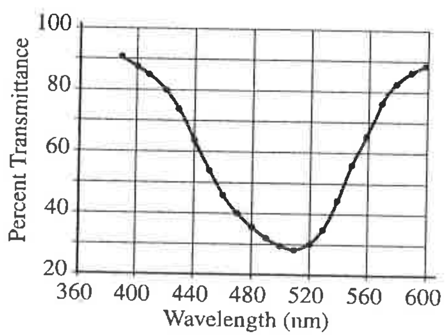
Your responses to the rest of the questions in this part of the examination will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

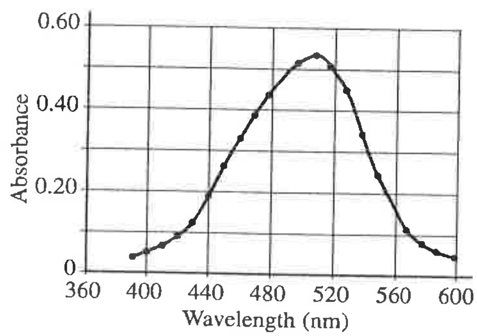
Answer BOTH Question 5 below AND Question 6 printed on page 12. Both of these questions will be graded. The Section II score weighting for these questions is 30 percent (15 percent each).

5. A student is instructed to determine the concentration of a solution of $CoCl_2$ based on absorption of light (spectrometric/colorimetric method). The student is provided with a 0.10 *M* solution of $CoCl_2$ with which to prepare standard solutions with concentrations of 0.020 *M*, 0.040 *M*, 0.060 *M*, and 0.080 *M*.

(a) Describe the procedure for diluting the 0.10 *M* solution to a concentration of 0.020 *M* using distilled water, a 100 mL volumetric flask, and a pipet or buret. Include specific amounts where appropriate.

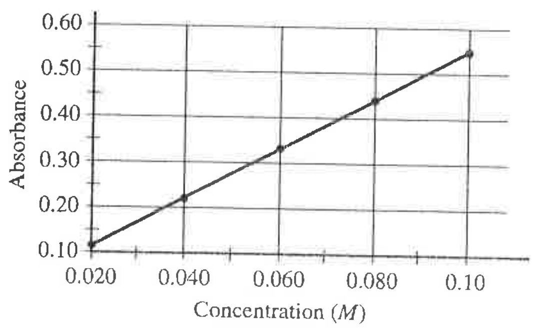
The student takes the 0.10 *M* solution and determines the percent transmittance and the absorbance at various wavelengths. The two graphs below represent the data.





(b) Identify the optimum wavelength for the analysis.

The student measures the absorbance of the 0.020 *M*, 0.040 *M*, 0.060 *M*, 0.080 *M*, and 0.10 *M* solutions. The data are plotted below.



(c) The absorbance of the unknown solution is 0.275. What is the concentration of the solution?

(d) Beer's Law is an expression that includes three factors that determine the amount of light that passes through a solution. Identify two of these factors.

(e) The student handles the sample container (e.g., test tube or cuvette) that holds the unknown solution and leaves fingerprints in the path of the light beam. How will this affect the calculated concentration of the unknown? Explain your answer.

(f) Why is this method of determining the concentration of $CoCl_2$ solution appropriate, whereas using the same method for measuring the concentration of NaCl solution would not be appropriate?

Answer on separate sheets

2004

ANSWER on Separate sheets

3. The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of 5.00×10^3 cm^{-1} M^{-1} and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

(a) Calculate the initial concentration of the colored species.

(b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.

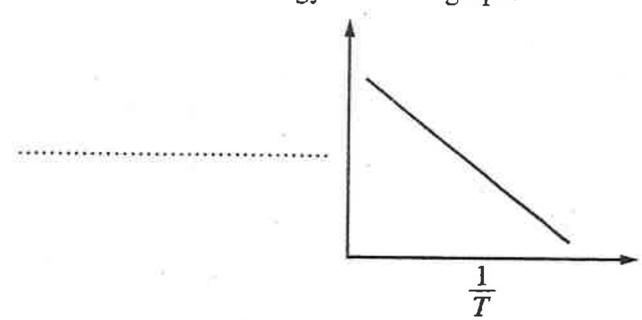
(c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.

(d) Calculate the half-life of the reaction. Include units with your answer.

* (e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy, E_a, of the reaction.

(i) Label the vertical axis of the graph.

(ii) Explain how to calculate the activation energy from this graph.



*See 11.5 in your book.