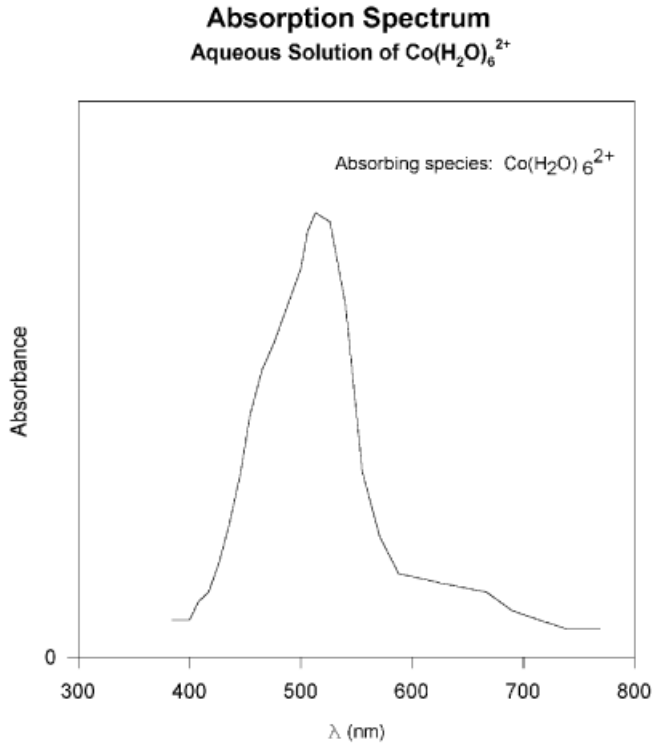
VII. Spectrophotometry

A) Absorption Spectrum

A *spectrophotometer* is an instrument that measures the amount of light absorbed by a substance.

An *absorption spectrum* is the plot of the absorbance versus the wavelength of the incident light.

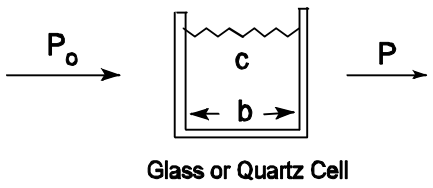
Example: Absorption spectrum of an aqueous soluton of $Co(H_2O)_6^{2+}$



B) Beer-Lambert Law (Beer's Law)

1) $A = \varepsilon bc$

The amount of light absorbed by a solution is an exponential function of the concentration of the absorbing species.



where P_o is the radiant power (energy/area-sec) of the incident light of known wavelength, P is the radiant power of the light after it has been transmitted through the solution, c is the molarity (moles of solute/liters of solution) of the absorbing species, and b is the path length.

Beer's Law

$$-\log\left[\frac{P}{P_o}\right] = \varepsilon b c$$

where ε is a constant called the *molar absorptivity*. The magnitude of ε depends on the wavelength of the incident, monochromatic light and the nature of the absorbing species.

Transmittance (T): $T = \dfrac{P}{P_o}$

Percent Transmittance (%T): $\%T = (T)(100)$

Absorbance (A): $A = -\log(T) = 2.00 - \log(\%T)$

$A = \varepsilon b c$ *or* $2.00 - \log(\%T) = \varepsilon b c$

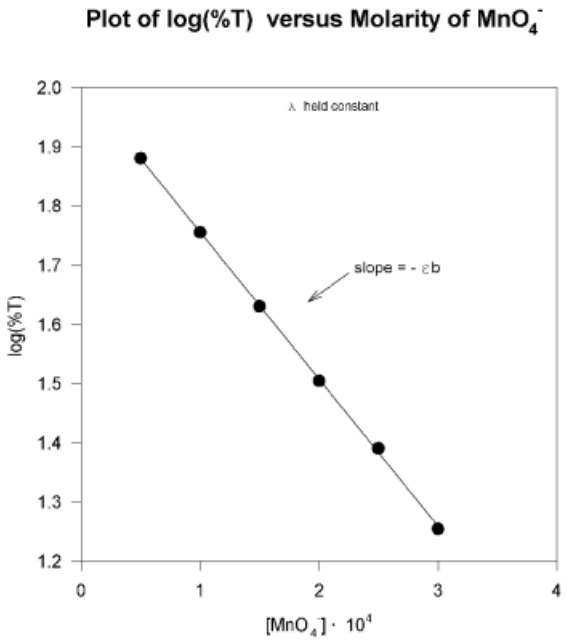
Note: When λ and b are held constant, then ε is constant and A or log(%T) varies linearly with c. The plot of A or log(%T) versus c at constant λ yields a calibration curve.

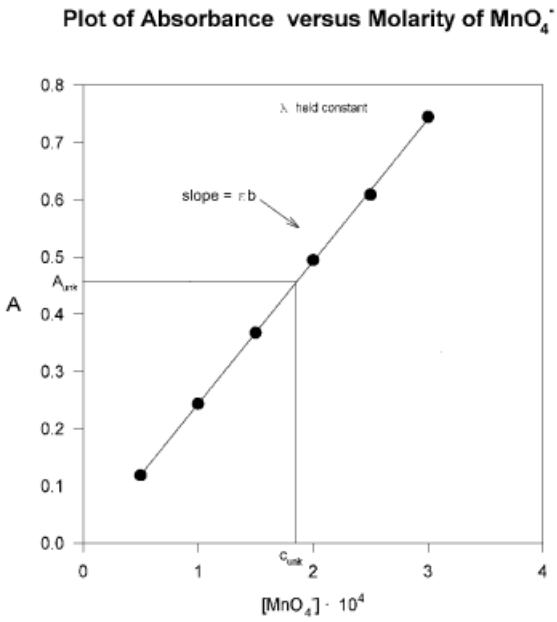
When c and b are held constant, then ε and hence A varies with λ. The plot of A versus λ at constant c and b gives an absorption spectrum.

2) Calibration Curve

Plot of A or log(%T) versus c at a specific λ

Example: Calibration Curves for Aqueous Solutions of MnO_4^-





where $[MnO_4^-] \cdot 10^4 = 1.5$ means that $[MnO_4^-] = 1.5 \cdot 10^{-4}$ M.

Use the calibration curve to verify that the absorbing species obeys Beer's Law. If the plot of log(%T) or A versus c gives a straight line, then Beer's Law is said to hold for the absorbing species.

Use the calibration curve to assist in the determination of the "unknown" molarity of the absorbing species in other solutions. To determine the "unknown" concentration of an absorbing species in a solution, measure the absorbance (A_{unk}) of the solution and read the concentration (c_{unk}) from the calibration curve (see example above).

3) Deviations for Beer's Law

The absorbance at a constant λ does **not** vary linearly with molarity.

a) Chemical (Apparent) Deviation

Occurs when the absorbing speices is involved in a concentration dependent dissociative or associative reaction or in a reaction with the solvent

Example: Consider the absorbing species D that dissociates into B and C in aqueous solutions.

$$D\ (aq) \rightleftharpoons B\ (aq) + C\ (aq)$$

$$A = \varepsilon b[D]_{eq} = \varepsilon b\left([D]_{in} - \frac{\sqrt{K^2 + 4K[D]_{in}} - K}{2}\right) \quad (1)$$

where

$$K = \frac{[B]_{eq}[C]_{eq}}{[D]_{eq}}$$

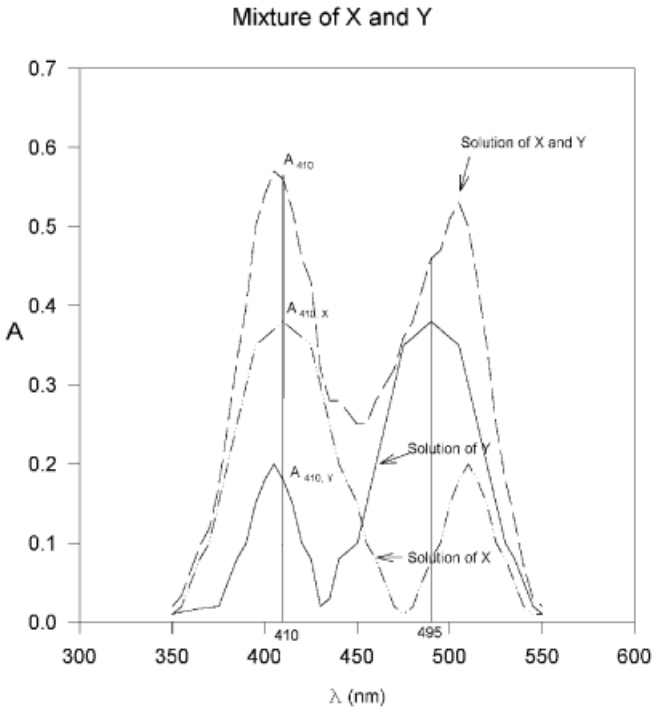
Although D obeys Beer's Law, the absorbance, A, does not vary linearly with the initial molarity of D (eq 1). When solvent is added to a solution of D, the $[D]_{in}$ decreases but $[D]_{eq}$ does not decrease linearly with $[D]_{in}$ due to the equilibrium.

b) Polychromatic Light

Beer's Law is valid only when monochromatic light is used. The incident light in most spectrophotometers is polychromatic with an effective bandwidth, $\Delta\lambda$, of 10 nm or greater. For this reason absorbance measurements are made in the region of the absorption spectrum where A changes little with a change in λ, usually at a maximum.

C) Mixtures of Absorbing Species

When two or more absorbing species are present in a solution, the absorbance of the solution at a specific λ is the sum of the absorbances of all the species provided that the species absorb at that λ.



At λ = 410 nm

$$A_{410} = A_{410,X} + A_{410,Y} = \varepsilon_{410,X}\, b\, c_X + \varepsilon_{410,Y}\, b\, c_Y$$

At λ = 495 nm

$$A_{495} = A_{495,X} + A_{495,Y} = \varepsilon_{495,X}\, b\, c_X + \varepsilon_{495,Y}\, b\, c_Y$$

Two equations are required to determine the two unknowns, C_X and C_Y. The molar absorptivities of X at the selected wavelengths (410 and 495 nm) are determined from absorbance measurements of a solution with a known amount of X (*solution of X*). The molar absorptivities of Y are obtained from absorbance measurements of a solution with a known amount of Y (*solution of Y*).

D) Analytical Procedure

To determine the concentration of an absorbing species in a sample solution,

- Obtain an absorption spectrum of the absorbing species to be studied,
- Select the wavelength λ at which the absorbance measurements for the calibration curve will be made,
  Usually λ is selected at a maximum in the absorption spectrum. Reasons:
  - Greatest change in absorbance with change in molarity of the absorbing species
  - Least change in absorbance with change in λ
- Determine if other species in the sample solution absorb at the chosen wavelength,
- Prepare a calibration curve,
  A set of standard solutions of the absorbing species are prepared and absorbances of these solutions are measured at the chosen wavelength. The absorbances are plotted as a function of the concentrations. The concentrations of the standard solutions are chosen so that the %T of these solutions lie in the range of 16 to 60% transmittance.
- And measure the absorbance of the sample solution at the chosen wavelength. The concentration of the sample solution may be obtained from the calibration curve.

E) Solution Calculations

Solute is the substance in a solution in the smaller amount.

Solvent is the substance in a solution in the larger amount.

$$Solute + Solvent \Rightarrow Solution$$

Example: Aqueous solution of silver nitrate

Silver nitrate ($AgNO_3$) is the solute and water is the solvent.

Concentration expressed in molarity.

$$Molarity\ of\ Solute = Molarity = [solute] = c_{solute} = \frac{moles\ of\ solute}{liters\ of\ solution}$$

$$units: \frac{mole}{L} = M$$

To determine the number of moles in a given volume of solution,

$$moles\ of\ solute = (Molarity)(liters\ of\ solution)$$

Example: How many liters of a 0.500 M $AgNO_3$ solution (*stock solution*) are needed to prepare 100 mL of a 0.200 M $AgNO_3$ solution (*new solution*)?

Step #1: Calculate the moles of solute needed for the new solution.

$$(mole\ solute) = (Molarity)_{new}\ (liters)_{new}$$

$$(mole\ AgNO_3) = (Molarity\ AgNO_3)_{new}\ (liters)_{new}$$

$$(mole\ AgNO_3) = (0.200\,M)(0.100\,L) = 2.00\cdot 10^{-2}\ mole\ AgNO_3$$

Step #2: Calculate the volume of the stock solution that gives the moles of solute needed for the new solution.

$$(liters)_{stock} = \frac{(mole\ solute)}{(Molarity)_{stock}}$$

$$(liters)_{stock} = \frac{(mole\ AgNO_3)}{(Molarity\ AgNO_3)_{stock}}$$

$$(liters)_{stock} = \frac{(2.00\cdot 10^{-2}\ mole\ AgNO_3)}{(0.500\,M)_{stock}} = 4.00\cdot 10^{-2}\,L$$

Step #3: Add solvent to obtain the desired volume of the new solution.

$$40.0\,mL\ of\ a\ 0.500\,M\ AgNO_3\ solution + 60.0\,mL\ of\ H_2O \Rightarrow 100\,mL\ of\ a\ 0.200\,M\ AgNO_3\ solution$$

Since the number of moles of solute is the same in Steps # 1 and #2,

$$(Molarity)_{new}\,(liters)_{new} \;=\; (Molarity)_{stock}\,(liters)_{stock}$$

Example: How many liters of a 0.500 M $AgNO_3$ solution (*stock solution*) are needed to prepare 100 mL of a 0.200 M $AgNO_3$ solution (*new solution*)?

$$(liters)_{stock} \;=\; \frac{(Molarity)_{new}\,(liters)_{new}}{(Molarity)_{stock}}$$

$$(liters)_{stock} \;=\; \frac{(Molarity\ AgNO_3)_{new}\,(liters)_{new}}{(Molarity\ AgNO_3)_{stock}} \;=\; \frac{(0.200\,M)(0.100\,L)}{(0.500\,M)}$$

$$(liters)_{stock} \;=\; 4.00\cdot 10^{-2}\,L$$