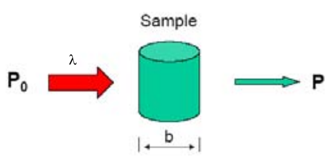
Chapter 24

Introduction to Spectrochemical Methods

Definition and Overview

- Spectroscopy:

A general term for the science that deals with various types of ***electromagnetic radiation*** (EMR) with *mater.*

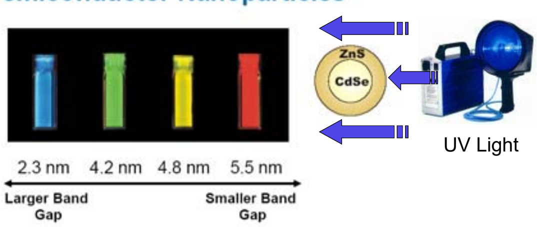


$$T = \frac{P}{P_o}$$

$$A = \log\frac{P_o}{P} = -\log T$$

$A = f(b, C)_\lambda$ Absorption Spectroscopy

Optical Properties of Semiconductor Nanoparticles

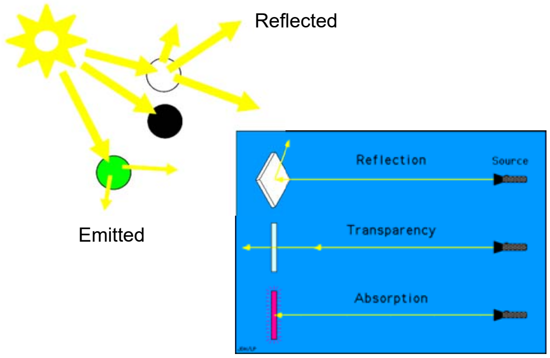


Courtesy of Bawendi and Coworkers.

$I = f(C)$

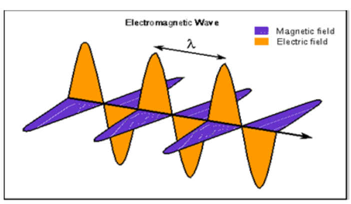
Emission Spectroscopy

Examples of EMR Interaction with Mater



Properties of Electromagnetic Radiation (EMR)

- an *oscillating* electric and magnetic field which travels through space (Waves!)

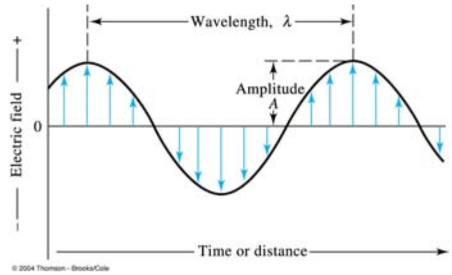


Also, EMR

--a discrete series of "particles" that have a specific energy but have no Mass (Particles!)

Waves + Particles

It Is a Wave!



Characterized by

λ—Wavelength, *A*—Amplitude, ν(nu)—Frequency

Wave Properties of EMR

The product of λ and ν is constant:

$\lambda \times \nu = c$

Since ν has units of sec^{-1}(hz) and λ has units of length,
their product, *c*, is the *velocity* of the wave:

- **in a vacuum**, all EMR travels at a velocity of:
2.99792458 x 10^8 m/s (= *c*)
("The Speed of Light")

$C = 3\times10^8$ m/s = 3×10^{10} cm/s = 3×10^{17} nm/s = 3×10^{18} Å/s

- Wavenumber

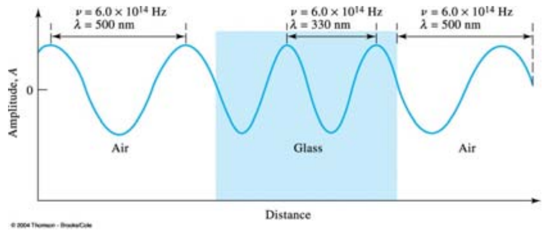
$\bar{\nu} = 1/\lambda$

–the number of waves per centimeter

$\bar{\nu}$ has the units of cm^{-1}

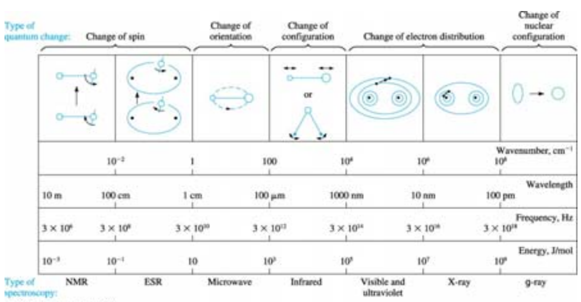
Propagation Velocity

- *What happens as an EMR wave propagates from a vacuum into another medium?*

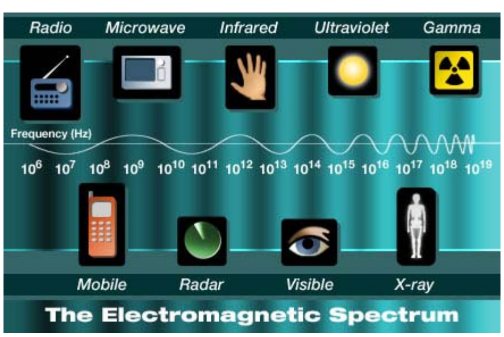


ν ***unchanged***; λ *decreases*; velocity *decreases*.

EMR Spectrum



EMR covers *a wide range* of wavelengths and frequencies.



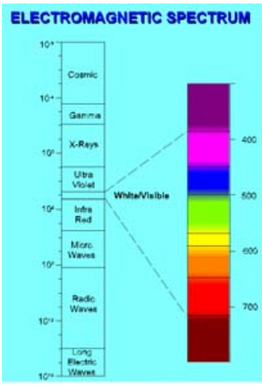


TABLE 24-2

Regions of the UV, Visible, and IR Spectrum

Region	Wavelength Range
UV	180–380 nm
Visible	380–780 nm
Near-IR	0.78–2.5 μm
Mid-IR	2.5–50 μm

Visible Light 380-780 nm

Particle Properties of EMR

- EMR: A beam of energetic particles ("photons").
- Photon are "destroyed" after absorption by a sample.
- Energy of a photon is related to its frequency.

$$E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

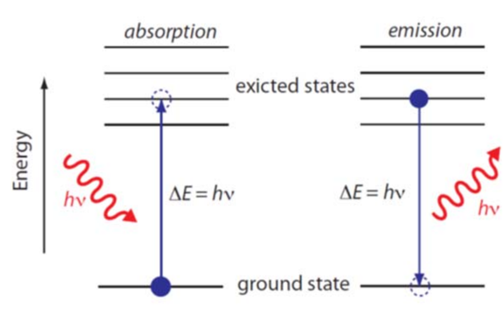
h is Plank's constant (6.63×10^{-34} J·s)

What is the energy of a photon from the sodium D line at 589 nm?

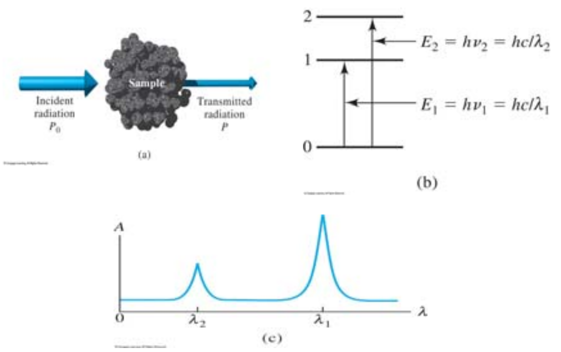
Solution

The photon's energy is

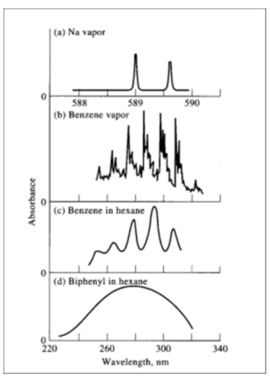
$$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{Js})(3.00\times10^{8}\,\text{m/s})}{589\times10^{-9}\,\text{m}} = 3.37\times10^{-19}\,\text{J}$$



Absorption Spectra

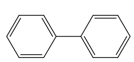


Absorption Spectra -Examples



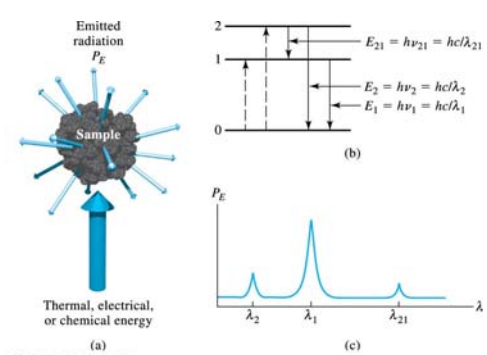
Line Spectrum

Band Spectrum

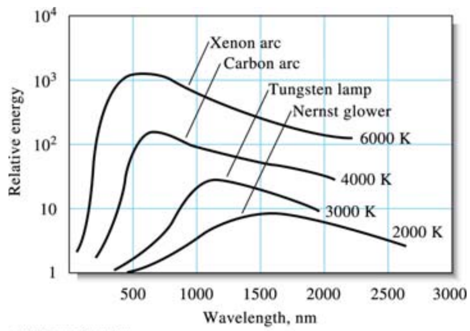


biphenyl

Emission/Luminescence Spectra

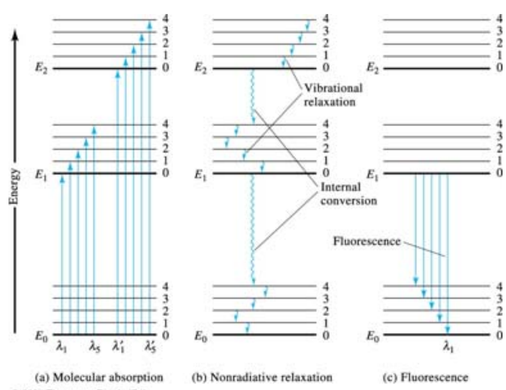


Thermal (Black body) Radiation

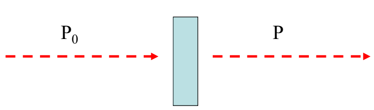


Heated to Incandescence

Transitions and Energy Levels



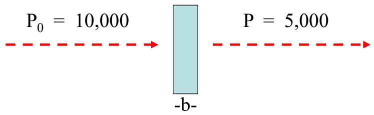
Absorption of Light – 1
Beer's Law



$$T = \frac{P}{P_0}$$

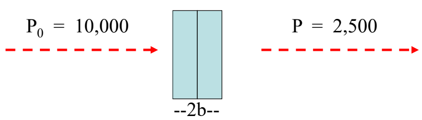
T: Transmittance

Absorption of Light – 2
Beer's Law



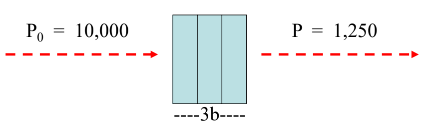
$$T = \frac{P}{P_0} = \frac{5000}{10000} = 0.5$$

Absorption of Light – 3
Beer's Law



$$T = \frac{P}{P_0} = \frac{2500}{10000} = 0.25$$

Absorption of Light – 4
Beer's Law



$$T = \frac{P}{P_0} = \frac{1250}{10000} = 0.125$$

$$A = -\log T = -\log \frac{P}{P_0}$$

$$A = abc$$

A = absorbance
a = absorptivity
b = thickness
c = concentration

Color Wheel Complementary Colors

Roy G. Biv

R = Red (700 nm)

O = Orange (620 nm)

Y = Yellow (550 nm)

G = Green (510 nm)

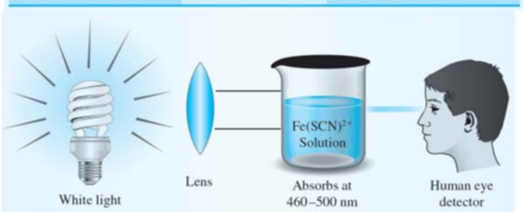
B = Blue (450 nm)

~~I = Indigo (450-425 nm)~~

V = Violet (410 nm)

The Visible Spectrum

Wavelength Region Absorbed, nm	Color of Light Absorbed	Complementary Color Transmitted
400–435	Violet	Yellow-green
435–480	Blue	Yellow
480–490	Blue-green	Orange
490–500	Green-blue	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Blue
595–650	Orange	Blue-green
650–750	Red	Green-blue



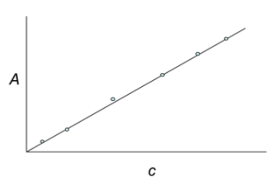
Beer's Law

$$A^{\lambda} = -\log T^{\lambda} = -\log[\frac{P}{P_0}]_{\lambda}$$

$$A^{\lambda} = a_{\lambda}bc = \varepsilon_{\lambda}bc$$

A = absorbance
a = absorptivity
b = thickness
c = concentration
ε = molar absorptivity

When *b* in cm, *c* in mol/L, *a* is called molar absorptivity and is given the special symbol *ε* (in L/(mol cm))



Beer's Law for Mixture-Additive

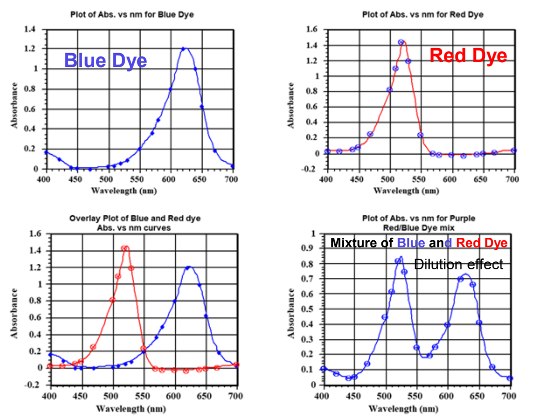
At any given wavelength of EMR absorption:

$A^{\lambda} = \varepsilon^{\lambda} bc$, for a mixture with n components,

the total A^{λ}_{Total} :

$$A^{\lambda}_{Total} = A^{\lambda}_{1} + A^{\lambda}_{2} + ...A^{\lambda}_{3} = \sum_{i=1}^{n} A^{\lambda}_{i} = \sum_{i=1}^{n} \varepsilon_i^{\lambda} bc_i$$

Example:
Mixture of Co(II), Cr(III), Ni(II), Cu(II)



Example:

The concentrations of Fe^{3+} and Cu^{2+} in a mixture are determined following their reaction with hexacyanoruthenate (II), $Ru(CN)_6^{4-}$, which forms a purple-blue complex with Fe^{3+} (λ_{max} = 550 nm) and a pale-green complex with Cu^{2+} (λ_{max} = 396 nm). The molar absorptivities (M^{-1} cm^{-1}) for the metal complexes at the two wavelengths are summarized in the following table.

	ε_{550}	ε_{396}
Fe^{3+}	9970	84
Cu^{2+}	34	856

When a sample that contains Fe^{3+} and Cu^{2+} is analyzed in a cell with a pathlength of 1.00 cm, the absorbance at 550 nm is 0.183 and the absorbance at 396 nm is 0.109. What are the molar concentrations of Fe^{3+} and Cu^{2+} in the sample?

Solution:

$$A_{550} = 0.183 = 9970C_{Fe} + 34C_{Cu}$$
$$A_{396} = 0.109 = 84C_{Fe} + 856C_{Cu}$$

To determine C_{Fe} and C_{Cu} we solve the first equation for C_{Cu}

$$C_{Cu} = \frac{0.183 - 9970C_{Fe}}{34}$$

and substitute the result into the second equation.

$$0.109 = 84C_{Fe} + 856 \times \frac{0.183 - 9970C_{Fe}}{34}$$
$$= 4.607 - (2.51 \times 10^5)\,C_{Fe}$$

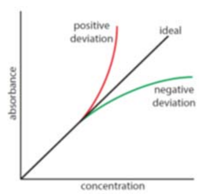
Solving for C_{Fe} gives the concentration of Fe^{3+} as 1.8×10^{-5} M. Substituting this concentration back into the equation for the mixture's absorbance at 396 nm gives the concentration of Cu^{2+} as 1.3×10^{-4} M.

Limitations to Beer's law

1. Concentration Limit: ≤ 0.10 M.

(a) At higher *c* the individual particles of analyte no longer are independent of each other- changing the ε value.

(b) The ε value depends on the solution's refractive index that varies with the *c*.



Limitations to Beer's law

2. Chemical limitations when chemical reactions occur.

Example: different *c* of a weak acid dissociation in water (acid-base indicators)

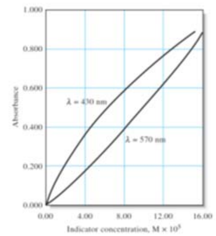
HIn (Color 1, in acid) = H^+ + In^- (Color 2)

Increase total $[HIn]_{total}$, [HIn] and $[In^-]$ increase non-linearly.

TABLE 24-4

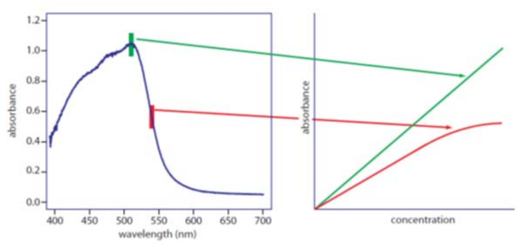
Absorbance Data for Several Concentrations of the Indicator in Example 24-5

c_{HIn}, M	[HIn]	[In^-]	A_{430}	A_{570}
2.00×10^{-5}	0.88×10^{-5}	1.12×10^{-5}	0.236	0.073
4.00×10^{-5}	2.22×10^{-5}	1.78×10^{-5}	0.381	0.175
8.00×10^{-5}	5.27×10^{-5}	2.73×10^{-5}	0.596	0.401
12.0×10^{-5}	8.52×10^{-5}	3.48×10^{-5}	0.771	0.640
16.0×10^{-5}	11.9×10^{-5}	4.11×10^{-5}	0.922	0.887



Limitations to Beer's law

3. Instrumental limitations.

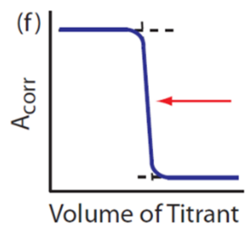


- Beer's Law Should be used Only for a Single Wavelength Incident Light.
- It is the basis of quantitative Analysis of Absorption Spectroscopy.

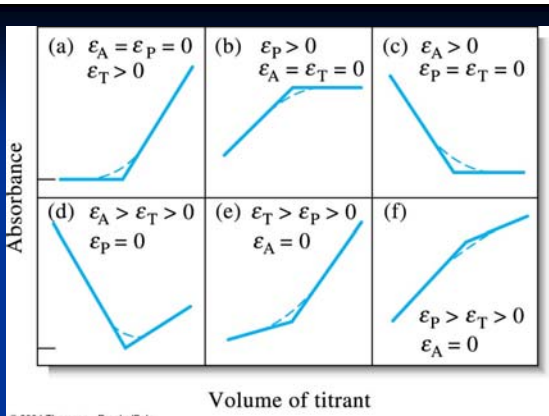
Photometric Titrations

- A photometric titration curve is a plot of absorbance as a function of the volume of titrant.
- The spectrometer detects the color change of an indicator allowing the endpoint to be accurately determined.
- For example: titration of an acid and base using phenolphthalein clear → pink

$$A + T \xrightleftharpoons{\text{Indicator}} P$$



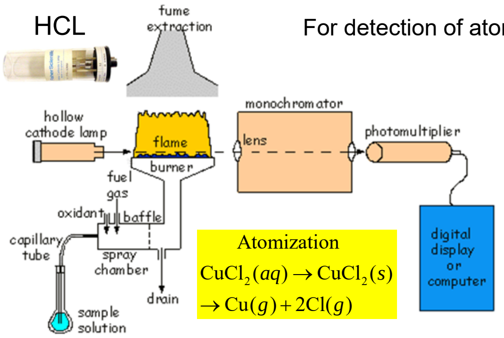
Only the indicator absorbs



Atomic Absorption Spectrometer

HCL

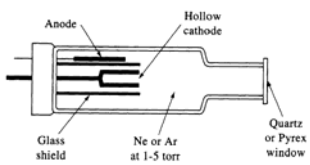
For detection of atoms



Atomization

$CuCl_2(aq) \rightarrow CuCl_2(s)$
$\rightarrow Cu(g) + 2Cl(g)$

Hollow Cathode Lamps



Hamamatsu Produces ~186 HCL Lamps

Can be used to detect ~70 metals