Sawa University

Analytical Chemistry

SPECTROSCOPY (THEORY)

Sawa University

College of Pharmacology

First Stage

جامعـــــة ســـــــاوة الأهلية

كلية الصيدلة

المرحلـــــــــــة الاولى

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المحاضرة الثامنة: الجانب النظري

Basic principles

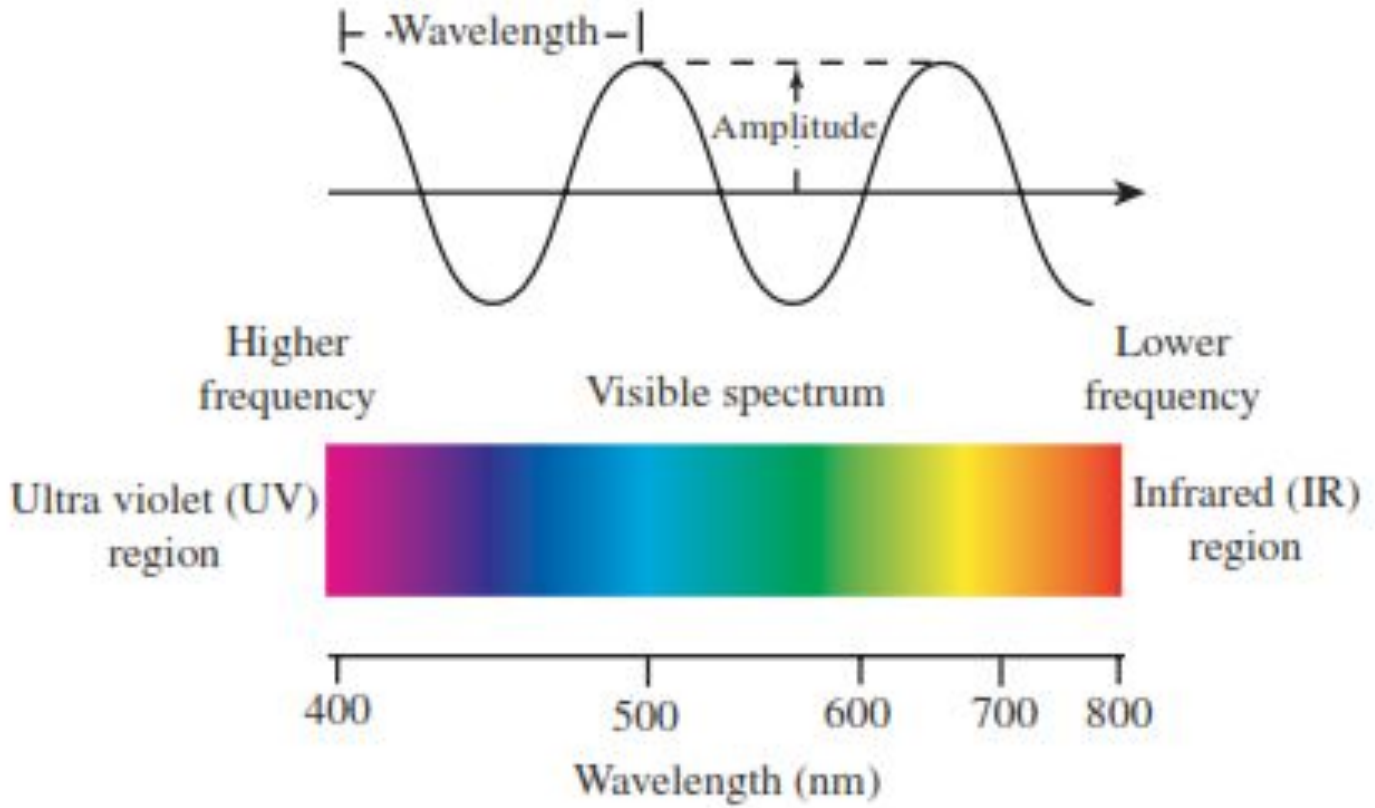
Wave and Particle Theory of Light

- Visible light electromagnetic radiation is described in a dual manner as a **wave phenomenon** (**wave theory**), characterized by a **wavelength** or **frequency** which is required to describe **optical** effects such as diffraction and refraction.
- Light is also described by a **particle phenomenon (particle theory)**, which is required to describe the **absorption and emission** of radiant energy.

Q/ The two theory to describe the light are…….and…… theory?
Q/ The wave theory describe …… effects such as diffraction and refraction?
Q/ The particle theory describe …… and …… of radiant energy?

Basic principles

- The "**wavelength**" **is the distance between adjacent peaks** (or troughs), and may be designated in meters, centimeters, or nanometers (10^{-9}m).
- The "**frequency**" **is the number of wave cycles** that travel past a fixed point **per unit of time** and is usually given in cycles per second, or hertz (Hz).



Q/ Define The wavelength?
Q/ Define The frequency ?

Basic principles

- The energy carried by a **photon** of a certain wavelength is proportional to its frequency. The following equations describe these relationships:

where
ν = *frequency*
λ = *wavelength*
c = *velocity of light* ($c = 3 \times 10$ cm/s).

$$\nu = \frac{c}{\lambda}$$

$$\Delta E = h\nu$$

E = *energy*
v* = *frequency
h = *Planck's constant* ($h = 6.6 \times 10^{-27}$ erg s)

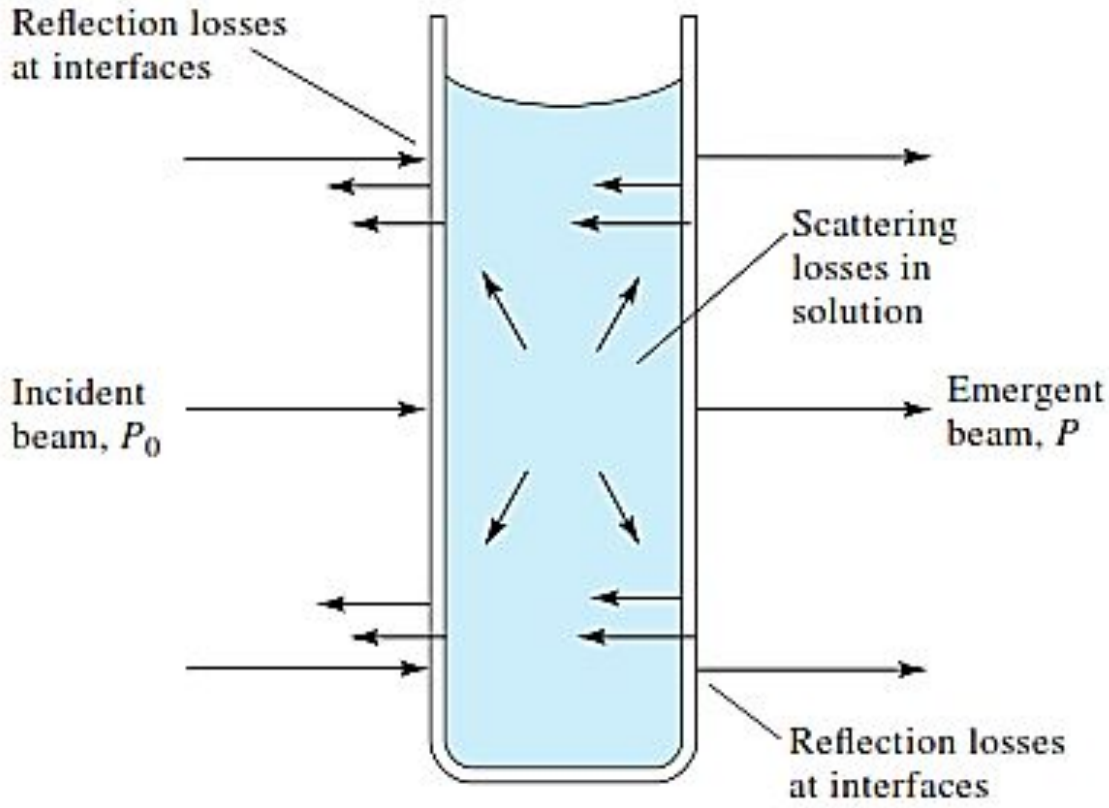
$$\Delta E = h\frac{c}{\lambda}.$$

Q/ In electromagnetic radiation the energy carried by …….?

Basic principles

Origin of UV-visible spectra

- When radiation interacts with matter, a number of processes can occur, including:
  - **Reflection**.
  - **Scattering.**
  - **Absorbance.**
  - **Fluorescence/phosphorescence** (absorption and reemission), and
  - **Photochemical reaction** (absorbance and bond breaking).



Q/ Numerical the process may be occur when radiation interact

Basic principles

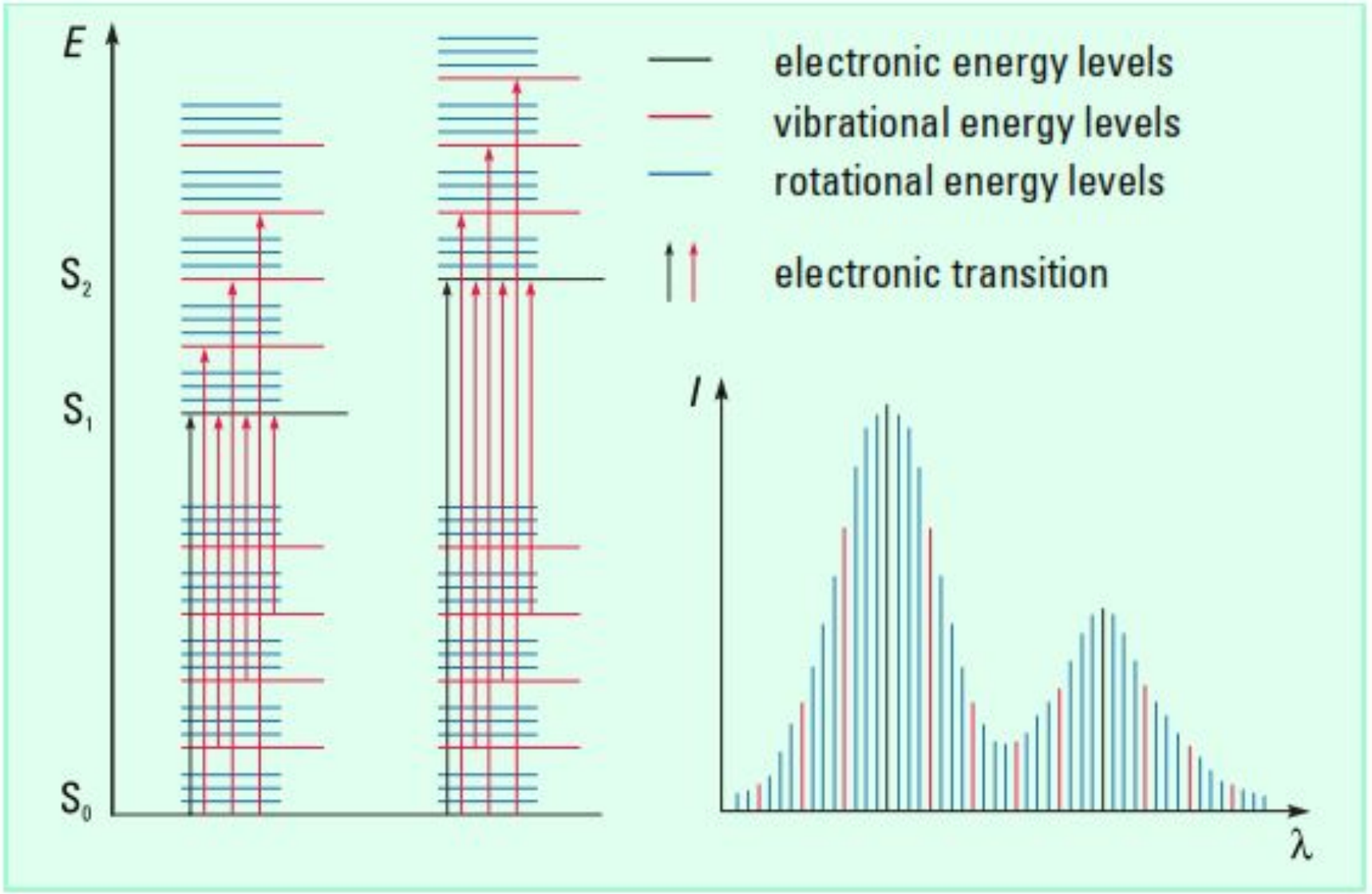
- Because light is a form of energy, absorption of light by matter causes the energy content of the molecules (or atoms) to increase.
- The total potential energy of a molecule generally is represented as the sum of its electronic, vibrational, and rotational energies.

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

- In some molecules and atoms, photons of UV and visible light have enough energy when interact with the matter **will cause transitions an electron between the different electronic energy levels where the electron from a lower energy level will move to a higher energy level.**

Q/ Explain what happen when photons of UV and visible light, have enough energy, interact with the matter?

Basic principles



Transmittance and absorbance

- When light passes through a sample, the amount of light absorbed **is the difference between the incident radiation (*I*) and the transmitted radiation (I_o).**
- The amount of light absorbed is expressed as either **transmittance** or **absorbance**.
- **Transmittance** usually is given in terms of a **fraction** or as a **percentage** and is defined as follows:

$$Transmittance = T = \frac{I}{I_o} \qquad Transmittance\% = T\% = \frac{I}{I_o} x\ 100$$

Transmittance and absorbance

- **Absorbance** is defined as follows:

$$Absorbance = A = -\log T = -\log \frac{I}{I_o} = \log \frac{I_o}{I}$$

Also

$$A = 2 - \log T\%$$

Example: Calculate the absorbance when the transmittance is 27.2%?

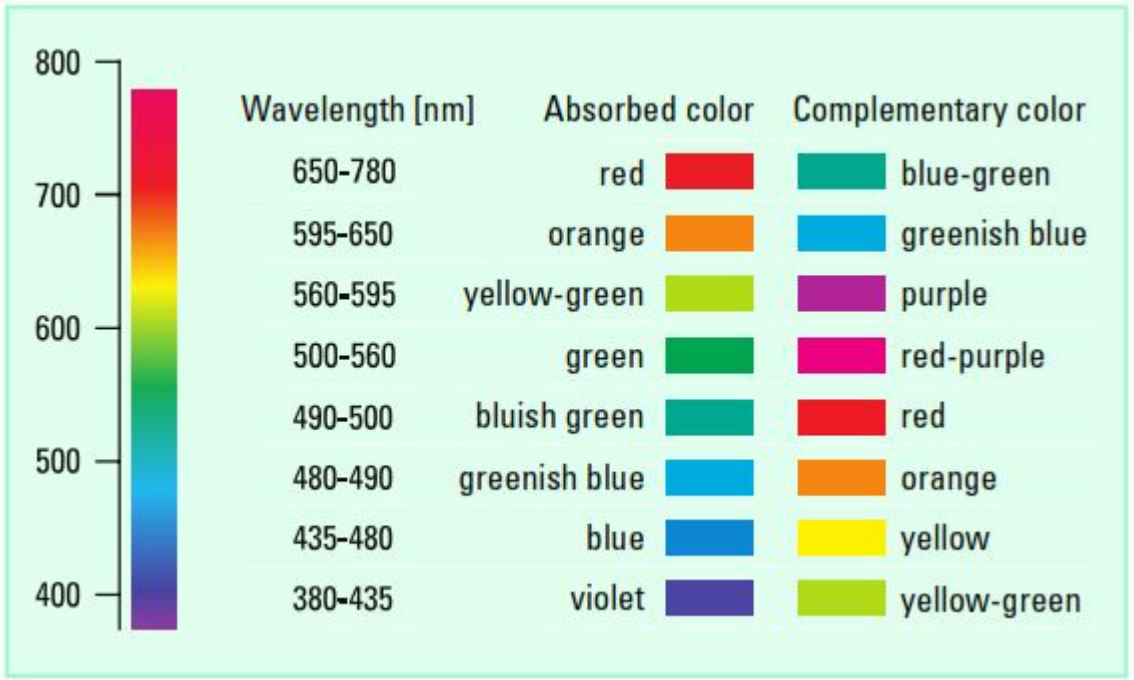
Solution:

$$A = 2 - \log T\%$$

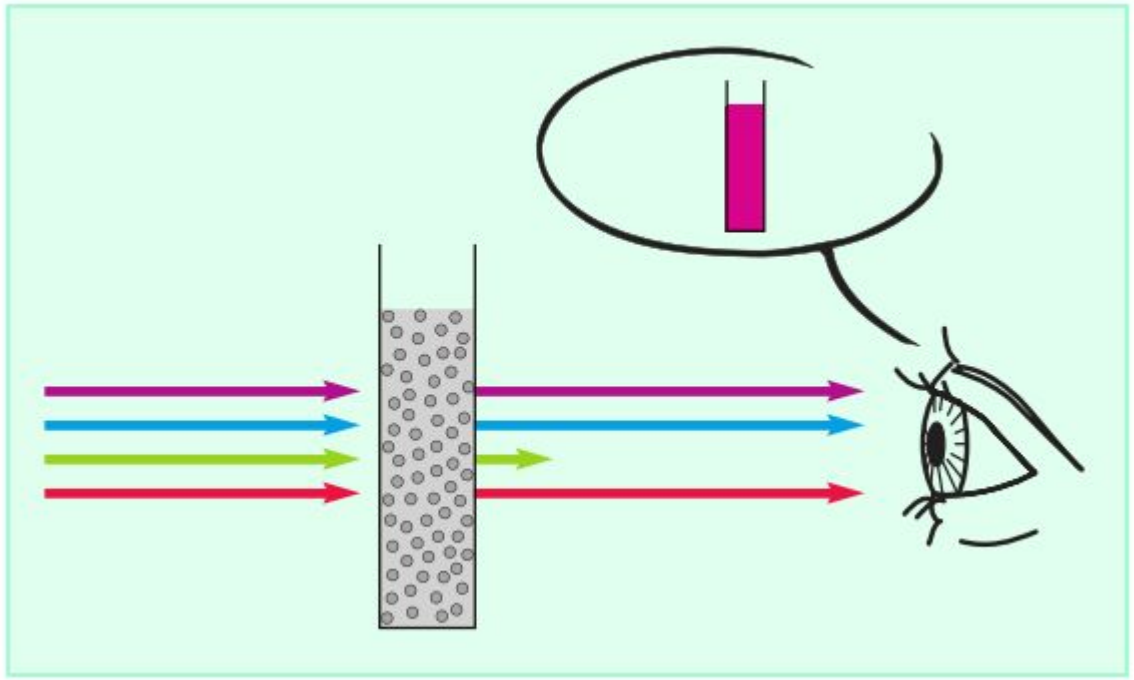
$$A = 2 - \log 27.2 = 2 - (1.434) = 2.565$$

Color

- Color is an important property of a substance.
- The color of matter is related to its absorptivity. The human eye sees the **complementary** color to that which is absorbed.



Wavelength [nm]	Absorbed color	Complementary color
650-780	red	blue-green
595-650	orange	greenish blue
560-595	yellow-green	purple
500-560	green	red-purple
490-500	bluish green	red
480-490	greenish blue	orange
435-480	blue	yellow
380-435	violet	yellow-green



Q/ If the solution absorb blue color, what the color can you see?

Q/ what the complementary color of the orange color?

Quantitative analysis

Beer's law

- The absorption law state , also known as the Beer-Lambert law or just Beer's law, is **(For a given material, the sample path length and concentration of the sample are directly proportional to the absorbance of the light)**.

$$A = \varepsilon c l$$

Where
A is absorbance
l is path length
ε is molar absorptivity (where e has the units of L mol^{-1} cm^{-1})

Q/ What does the beer's law state?

Quantitative analysis

Beer's law

Example 1:

A 7.25 x 10^{-5} M standard solution of potassium permanganate has a transmittance of 44.1% when measured in a 2.10-cm cell at a wavelength of 525 nm. Calculate (a) the absorbance of this solution and (b) the molar absorptivity of $KMnO_4$.

Solution:

(a)

$$A = 2\text{-}log\ T\ \% = 2\text{- log } 44.1 = 2\text{-}1.644 = 0.356$$

(b)

$$A = \varepsilon cl \gg \varepsilon = \frac{A}{cl} = \frac{0.356}{7.25 \text{ x } 10^{-5}\ x\ 2.10} = 2.34 \text{x } 10^{3}\ \text{L mol}^{-1}\ \text{cm}^{-1}$$

Quantitative analysis

Beer's law

Example 2:

The another of the same solution of potassium permanganate (unknown concentration) which absorb 0.45. Calculate the concentration of the unknown?

Solution:

$$A = \varepsilon c l \gg c = \frac{A}{\varepsilon l} = \frac{0.45}{2.34\text{x } 10^{3}\ x\ 2.1} = 0.9\ x\text{x } 10^{-4}$$

Quantitative analysis

Beer's law

Another solution:

Where the solution is same therefore ε is the same for the two solution, therefor can derive one equation for calculate the concentration of the unknown when the absorbance of the unknown and standard is known?.

$$A_{unknwon} = \varepsilon c_{unknwon} l$$

$$A_{standard} = \varepsilon c_{standard} l$$

$$\frac{A_{unknwon}}{A_{standard}} = \frac{\varepsilon c_{unknwon} l}{\varepsilon c_{standard} l} = \frac{c_{unknwon}}{c_{standard}}$$

$$c_{unknwon} = \frac{A_{unknwon}}{A_{standard}} \, x c_{standard}$$

$$c_{unknwon} = \frac{0.45}{0.356} \, x 7.25 \text{ x } 10^{-5} = 0.9 \, x \text{x } 10^{-4}$$