Lambert-Beer's law

The law was first developed by Pierre Bouguer before 1729. It was later attributed to Johann Heinrich Lambert who cited Bouguer’s findings. The law included path length as a variable that affected absorbance. Later, Beer extended in 1852 the law to include the concentration of solutions, thus giving the law its name Beer-Lambert Law.

Definition & Equation

- The Beer-Lambert law states that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.
- Because Beer's law states this, it means we can both calculate the concentration of a solution by using the absorbancies, or plot a graph of various concentrations, align them to their correct absorbencies, and use a colorimeter to find the concentration of an unknown solution
- The law states that:

  $A(\lambda) = e(\lambda)\ l\ c$.
  The proportionality constant $e\ (\lambda)$ is called the absorptivity of the substance at the wavelength λ. $e\ (\lambda)$ is called the molar absorptivity if the concentration is measured in moles/liter.

- The absorbance is inversely proportional to the transmittence of the solution

Derivation of Law

A spectrophotometer is an apparatus that measures the intensity, energy carried by the radiation per unit area per unit time, of the light entering a sample solution and the light going out of a sample solution. The two intensities can be expressed as transmittance: the ratio of the intensity of the exiting light to the entering light or percent transmittance ($\%T$). Different substances absorb different wavelengths of light. Therefore, the wavelength of maximum absorption by a substance is one of the characteristic properties of that material. A completely transparent substance will have $I_t = I_0$ and its percent transmittance will be 100. Similarly, a substance which allows no radiation of a particular wavelength to pass through it will have $I_t = 0$, and a corresponding percent transmittance of 0.

Transmittance

$T = I_t / I_0$
% Transmittance: $\%T = 100\ T$

Absorbance

$A = \log10\ (I_0/I_t)$
$A = \log10\ (1/T) = -\log10\ (T)$
$A = \log10\ (100/\%T)$
$A = 2 - \log10\ (\%T)$

Transmittance for liquids is usually written as: $T = I/I_0 = 10^{-\alpha l} = 10^{\Sigma lc'}$,
Transmittance for gases is written as $T = I/I_0 = 10^{-\alpha}l = e^{-\sigma lN}$
I_0 and I are the intensity (or power) of the incident light and the transmitted light, respectively.
Absorbance for liquids is written as $A = -\log10 = (I/I_0)$
Absorbance for gases it is written as $A' = -\ln(I/I_0)$

Deviations to the law

The Beer-Lambert law maintains linearity under specific conditions only. The law will make inaccurate measurements at high concentrations because the molecules of the analyte exhibit stronger intermolecular and electrostatics interactions which is due to the lesser amount of space between molecules. This can change the molar absorptivity of the analyte. Not only does high concentrations change molar absorptivity, but it also changes the refractive index of the solution causing departures from the Beer-Lambert law.

Applications

Beer-Lamberts law is applied to the analysis of a mixture by spectrophotometry, without the need for extensive pre-processing of the sample. Examples include the determination of bilirubin in blood plasma samples. The spectrum of pure bilirubin is known thus the molar absorbance is known. Measurements are made at one specific wavelength almost unique for bilirubin and another measurement at a second wavelength so interferences or deviations can be eliminated or corrected. Generally, it can be used to determine concentrations of a particular substance, or determine the molar absorptivity of a substance.

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