1.4: Absorbance and Concentration

When monochromatic electromagnetic radiation passes through an infinitesimally thin layer of sample of thickness *dx*, it experiences a decrease in its power of *dP* (Figure 1.4.1).

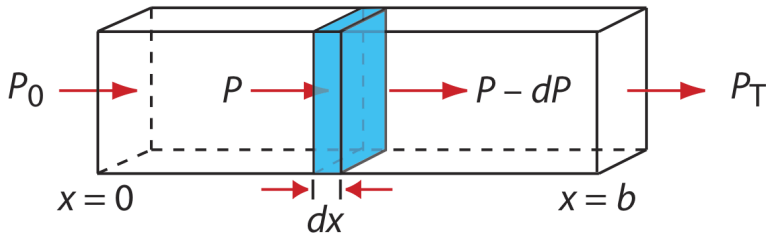

Figure 1.4.1. Factors used to derive the Beer's law.

This fractional decrease in power is proportional to the sample's thickness and to the analyte's concentration, *C*; thus

$$-\frac{dP}{P} = \alpha C dx \tag{1.4.1}$$

where *P* is the power incident on the thin layer of sample and α is a proportionality constant. Integrating the left side of Equation 1.4.1 over the sample's full thickness

$$-\int_{P=P_0}^{P=P_t} \frac{dP}{P} = \alpha C \int_{x=0}^{x=b} dx$$

$$\ln \frac{P_0}{P_T} = \alpha b C$$

converting from ln to log, and substituting into the equation relating transmittance to absorbance

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

gives

$$A = abC \tag{1.4.2}$$

where *a* is the analyte's absorptivity with units of cm^{-1} $conc^{-1}$. If we express the concentration using molarity, then we replace *a* with the molar absorptivity, ε, which has units of cm^{-1} M^{-1}.

$$A = \varepsilon b C \tag{1.4.3}$$

The absorptivity and the molar absorptivity are proportional to the probability that the analyte absorbs a photon of a given energy. As a result, values for both *a* and ε depend on the wavelength of the absorbed photon.

Example 1.4.1

A 5.00×10^{-4} M solution of analyte is placed in a sample cell that has a pathlength of 1.00 cm. At a wavelength of 490 nm, the solution's absorbance is 0.338. What is the analyte's molar absorptivity at this wavelength?

Solution

Solving Equation 1.4.3 for ϵ and making appropriate substitutions gives

$$\varepsilon = \frac{A}{bC} = \frac{0.338}{(1.00 \text{ cm})\left(5.00 \times 10^{-4} \text{ M}\right)} = 676 \text{ cm}^{-1} \text{ M}^{-1}$$

Exercise 1.4.1

A solution of the analyte from Example 1.4.1 has an absorbance of 0.228 in a 1.00-cm sample cell. What is the analyte's concentration?

Answer

Making appropriate substitutions into Beer's law

$$A = 0.228 = \varepsilon b C = \left(676\ \text{M}^{-1}\ \text{cm}^{-1}\right)(1\ \text{cm})C$$

and solving for *C* gives a concentration of 3.37×10^{-4} M.

Equation 1.4.2 and Equation 1.4.3, which establish the linear relationship between absorbance and concentration, are known as Beer's law. Calibration curves based on Beer's law are common in quantitative analyses.

As is often the case, the formulation of a law is more complicated than its name suggests. This is the case, for example, with Beer's law, which also is known as the Beer-Lambert law or the Beer-Lambert-Bouguer law. Pierre Bouguer, in 1729, and Johann Lambert, in 1760, noted that the transmittance of light decreases exponentially with an increase in the sample's thickness.

$$T \propto e^{-b}$$

Later, in 1852, August Beer noted that the transmittance of light decreases exponentially as the concentration of the absorbing species increases.

$$T \propto e^{-C}$$

Together, and when written in terms of absorbance instead of transmittance, these two relationships make up what we know as Beer's law.

Limitations to Beer's Law

Beer's law suggests that a plot of absorbance vs. concentration—we will call this a Beer's law plot—is a straight line with a *y*-intercept of zero and a slope of *ab* or εb. In some cases a Beer's law plot deviates from this ideal behavior (see Figure 1.4.2), and such deviations from linearity are divided into three categories: fundamental, chemical, and instrumental.

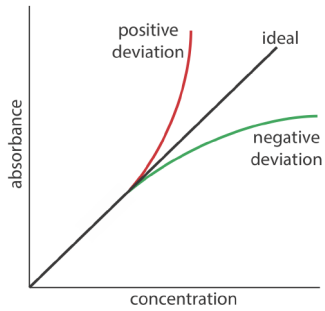

Figure 1.4.2. Plots of absorbance vs. concentration showing positive and negative deviations from the ideal Beer's law relationship, which is a straight line.