# Beer's law

A beam of light of intensity $I_0$ goes through a homogeneous dilute solution of absorbers "A" with concentration $[A]$. The light gets attenuated as it goes through the cell of length $\ell$ and exits with intensity $I < I_0$. We want to calculate $I$ or $I_{abs} = I_0 - I$.

Let's say the light travels along $x$, with $x = 0$ at the entry point into the solution, and $x = \ell$ at the exit point: $\ell$ is the path length. At $x = 0$, $I = I_0$. The probability that a photon of the beam gets absorbed between $x = 0$ and $x = dx$ is Prob$\propto [A]dx$ or Prob$= \epsilon[A]dx$, where $\epsilon$ is the proportionality factor which depends on the molecule "A" absorbing light and the wavelength $\lambda$. The attenuation factor between $x = 0$ and $x = dx$ is $(1 - \epsilon[A]dx)$, and the intensity of light at $x = dx$ is

$$I(dx) = I_0(1 - \epsilon[A]dx)$$

The attenuation factor is also $(1 - \epsilon[A]dx)$ for $x = dx$ to $x = 2dx$, and for $x = 2dx$ to $x = 3dx$, and so on. So

$$\begin{aligned} I(2dx) &= I_0(1 - \epsilon[A]dx)^2 \\ I(3dx) &= I_0(1 - \epsilon[A]dx)^3 \\ &\dots \end{aligned}$$

Then, $I(\ell) \equiv I = I_0(1 - \epsilon[A]dx)^n$, or

$$I_0/I = (1 - \epsilon[A]dx)^{-n}$$

$$\ln(I_0/I) = -n\ln(1 - \epsilon[A]dx)$$

$$= -n(-\epsilon[A]dx - (\epsilon[A]dx)^2 - \ \dots\ )$$

In the limit $dx \to 0$ we have

$$\ln(I_0/I) = n\epsilon[A]dx$$

Since $n = \ell/dx$,

$$\ln(I_0/I) = \epsilon\ell[A]$$

Instead of $I_0/I$ or $I_{abs} = I_0 - I$, people sometimes write Beer's law in term of the *transmittance* $T = I/I_0$:

$$I/I_0 \equiv T = e^{-\epsilon\ell[A]}$$

Instead of natural logarithms, people sometimes use base-10 log, and a $\epsilon$ that is 2.303 times smaller:

$$T = 10^{-\epsilon\ell[A]} \equiv 10^{-A}$$
$$A = \epsilon\ell[A]$$

$A$ is called the *absorbance*. The derivation of Beer's law depends on the assumption that $[A]$ is sufficiently small (dilute solution). If $[A]$ is large, we could have A—A interactions and cooperative effects. If $[A]$ is small enough, we can further simplify Beer's law:

$$I_0/I = e^{\epsilon\ell[A]}$$
$$= 1 + \epsilon\ell[A] + \frac{1}{2}(\epsilon\ell[A])^2 + \dots$$

Keeping only the first two terms,

$$\begin{aligned} I_0/I &\approx I/I + \epsilon\ell[A] \\ I_0 - I &\approx I\epsilon\ell[A] \end{aligned}$$

When $[A]$ is very small, we normally have $I/I_0 \approx 1$ and we can write $I_{abs} = I_0 - I$ like this

$$I_0 - I \equiv I_{abs} \approx I_0\epsilon\ell[A]$$

or, if we use the $\log_{10}$ convention instead,

$$I_{abs} \approx 2.303 \times I_0\epsilon\ell[A]$$

with $\epsilon$ smaller by a factor 2.303.