Question #63695, Chemistry / Physical Chemistry

Derive mathematical form of beer lamberrt's law .at definite wave length,an absorber when placed in a cell of 1 cm path length absorbs 20% of the incident light.if the absorptivity of the absorber at this wavelength is 2.0, find out its concentration.

Solution*:*
Consider a beam of parallel monochromatic light with intensity I_0 striking the sample at the surface as shown in the figure above, such that it is perpendicular to the surface. After passing through the path length b of the sample, which contains N molecules/cm3, the intensity of the light reduces to I_T.
Now, consider a cross-section of the block having an area S and an infinitesimal thickness dz placed at a distance z from the surface.
If the sample has N molecules/cm^3, the number of molecules present in the infinitesimal block would be
$= N \times S \times dz$
If each molecule has a cross-sectional area σ, where photons of light get absorbed, then the fraction of the total area where light gets absorbed due to each molecule would be (fractional area for each molecule)
$= \sigma / S$.
The total fractional area for all molecules in the block where light gets absorbed would therefore be
= (number of molecules) × (fractional area for each molecule)
i.e.$= (N \times S \times dz) x (\sigma / S) = \sigma \times N \times dz$
If I_z is the light entering the infinitesimal block considered, and the light absorbed due to the absorbing particles is dI, the light exiting the slab would be $I_z - dI$.
The fraction of light absorbed would therefore be $= dI/I_z$
Now, since the fractional area is the probability of light striking a molecule,
the fraction of light absorbed in the block = fractional area occupied by all the molecules in the slab.
i.e. $dI / I_z = -\sigma \times N \times dz$
Note: The negative sign is placed to indicate absorption of light. If we integrate this infinitesimal block for the whole sample from z=0 to z=b, where b is the path length of the entire solution we get
$\ln I_T - \ln I_0 = -\sigma \times N \times b$
OR
$-\ln (I_T / I_0) = \sigma \times N \times b$
One can correlate the number of molecules/cm^3 of sample to the concentration of the sample in moles/liter using the relationship:
$c = N \times 1000/ (6.023 \times 10^{23})$
OR
$N = (6.023 \times 10^{23}) \times c / 1000 = 6.023 \times 10^{20} x c$
where c is the concentration in moles/litre, N is the number of molecules/cm^3, and (6.023 x 10^{23}) is the Avagadro's number. N × 1000 would be therefore molecules / liter as 1 liter = 1000 cm^3.
Substituting this term for N in the above equation we get:
$-\ln (I_T / I_0) = \sigma \times 6.023 \times 10^{20} \times c \times b$

To simplify this equation further we convert to log using the term 2.303 × log (x) = ln (x). therefore we get,

$– \log (I_T / I_0) = (\sigma \times 6.023 \times 10^{20} \times c \times b) / 2.303$

OR

$\log (I_0 / I_T) = [(\sigma \times 6.023 \times 10^{20})/2.303] \times c \times b$

The term $\log (I_0 / I_T)$ is nothing but absorbance (A). While the term in the brackets [ ] is a constant and can be replaced by a constant ε = (σ × 6.023 × 1020)/2.303. Thus we get:

A = ε × c × b

OR

A = εbc

$$A = \varepsilon \times c \times l$$

$$c = \frac{A}{\varepsilon \times l}$$

$$c = \frac{0.2}{2.0\ M^{-1}cm^{-1} \times 1\ cm} = \mathbf{0.1\ M}$$