Molar absorption rate coefficient -A short note

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Abstract: The molar absorption rate coefficient is a measure of how fast a chemical species absorbs light at a given wavelength. The prime objective of writing this paper is to outline a formula for the calculation of the molar absorption rate coefficient.
[Manjunath.R. **Molar absorption rate coefficient -A short note.** *N Y Sci J* 2012; 5(12):104-105]. (ISSN: 1554-0200). http://www.sciencepub.net/newyork. 16

Keywords: photon absorption; chemical species; molar absorption rate coefficient; refractive index.

Total number of photons of any monochromatic radiation falling on a homogeneous slab gets distributed into parts such as:

Number of photons reflected: N_r
Number of photons transmitted: N
Number of photons absorbed: N_a
We may write, $N_0 = N_r + N + N_a$

In most cases of homogeneous nonmetallic substances, such as transparent slabs, the loss of radiant photons due to reflection may not exceed 4%. This fraction can be, and is therefore, usually ignored.

Thus, for all practical purposes, we may write:

$$N_0 = N + N_a$$

As a parallel monochromatic beam of radiant photons passes through a homogeneous slab of thickness b of an absorber, the number of photons reduces from N_0 to N. Suppose dN is the change in number of photons in a small interval of time dt, the rate of photon absorption is expressed as,

$$\text{Rate of photon absorption} = -\, dN/dt$$

If temperature, pressure, wavelength and composition are held constant then the rate of photon absorption depends only on the number of photons traversing the slab. The rate of photon absorption typically follows first order kinetics. Mathematically, the above statement can be expressed as follows.

$$-\, dN/dt = k\,N$$

where k is the proportionality constant called absorption rate coefficient (also called specific absorption rate) and the negative sign indicates that radiant photons decreases with time.
This equation can be rearranged to:

$$d \ln N = -\, k\, d t$$

On integration within the limits of N_0 to N for number of photons and 0 to t for time we get,

$$\int_{N_0}^{N} d \ln N = -\, k \int_{0}^{t} d t$$

$$\text{Or} \quad \ln (N / N_0) = -\, k\, t$$

$$\text{Or} \quad \log (N_0 / N) = (k/2.303)\, t$$

Re- expressing in terms of intensity we get,

$$\log (I_0 / I) = (k/2.303)\, t$$

The term $\log (I_0 / I)$ is called absorbance and is represented as 'A'.

$$A = \log (I_0 / I)$$

The above expression then becomes,

$$A = (k/2.303)\, t$$

When monochromatic radiation travels in a homogeneous solution of refractive index η a distance b with a velocity (c/ η), then the time taken by radiation is $t = \eta\, b /c$

where $c = 3\times 10^{10}$cm/s (speed of light in vacuum)

Since

$$t = \eta\, b /c$$

we have

$$A = (k /2.303c)\, \eta\, b$$

When homogeneous solutions of chemical species are considered, it is clearly desirable to modify this expression to include the concentration of absorbing chemical species.

Thus, the absorption rate coefficient in above equation is in turn related to the concentration of absorbing chemical species.

$$k = k_m C$$

where k_m, called the molar absorption rate coefficient, is a proportionality constant determined by the nature of the absorbing solute and the wavelength of light used.

- k_m is a measure how fast a chemical species absorbs light at a given wavelength.

Replacing k by $k_m C$ we get,

$$A = (k_m / 2.303c)\ \eta\ b\ C$$

Or $$k_m = 2.303\ A\ c / \eta\ b\ C$$

Thus, we have the formula for the calculation of the molar absorption rate coefficient. This equation is strictly applicable only to optically transparent homogeneous solutions of chemical species.

In this expression, k_m is called molar absorption rate coefficient (also called molar extinction coefficient) whose value depends on unit of concentration used and is a function of refractive index of the absorbing solution used. The concentration is generally expressed in terms of moles per dm^3 and cell path length (b) in cm. Therefore, it has units of $dm^3\ mol^{-1}\ s^{-1}$. The absorbance is measured with some form of spectrophotometer. At present spectrophotometers utilizing photoelectric cells are available which give absorbance directly. Once absorbance for a given solution is measured and the thickness of the cell used is known, the molar absorption rate coefficient of the given solution for the given wavelength can readily be calculated by knowing the refractive index of the solution and the concentration of absorbing chemical species.

12/10/2012

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