Beer's law revisited

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Beer's Law Revisited

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Beer's law of light absorption is well known. Its derivation is given in most physical chemistry and instrumental analysis textbooks. It has also been heavily discussed in *this Journal*[1], the topics addressed being as diverse as history (*1, 6*), alternative derivations (*2–5, 7, 8, 10*), terminology and units (*2, 7, 15–17*), and applications (*13, 14, 17–20*). It may thus appear that no room is left for further discussion. However, this is certainly not the case with respect to the derivation of the law. In this work, a corpuscular derivation of Beer's law is given. The discussion of the law in these terms is advantageous because it provides more physical insight than the two common approaches that we shall here call classical and standard. For the sake of completeness these are briefly mentioned before the corpuscular one. Some aspects related with Beer's law are also discussed.

Classical Derivation (*21*)

When monochromatic light of intensity I passes through a slab of material of thickness dx, containing an absorbing species at a molar concentration C, there is an intensity loss given by

$$\mathrm{d}I = -\alpha C I \,\mathrm{d}x \tag{1}$$

Where the coefficient α is called the absorption coefficient and depends both on the species and wavelength. For a finite path l, and assuming the sample to have uniform concentration, integration of eq 1 yields Beer's law,

$$I = I_0 \exp(-\alpha C l) \tag{2}$$

This derivation is not especially illuminating, as the origin of eq 1 remains unclear, although it appears reasonable. (αI is the first nonzero term of the power series expansion of a more general functional dependence on intensity.)

Standard Derivation (*22*)

Regarding absorption as the capture of a photon by a molecule, each molecule has an associated capture area or cross section σ, whose magnitude is wavelength dependent. In the slab of thickness $\mathrm{d}x$, there are $\mathrm{d}N$ molecules,

$$\mathrm{d}N = N_A C S \mathrm{d}x \tag{3}$$

N_A being Avogadro's constant and S the slab cross section. Owing to the infinitesimal thickness of the slab (one molecule thick?) the total absorption cross section is simply the sum of all molecular cross sections, that is, $\sigma \mathrm{d}N$, hence the probability of photon capture within the slab is

$$\frac{-\mathrm{d}I}{I} = \frac{\sigma \mathrm{d}N}{S} = \sigma N_A C \,\mathrm{d}x \tag{4}$$

Therefore, the absorption coefficient α is simply the molecular one times Avogadro's constant. Owing to its molecular basis, this derivation provides a more perceptive picture than the previous one. Still, the continuum formulation was not abandoned. But do we really need to concentrate first on an "infinitesimally" thin slab and then, by integration, proceed to the finite one?

Corpuscular Derivation

Consider a pointlike photon and its linear path across the sample (figure). If the molecular cross section is assumed to be circular, the photon can pass through only if no circle centers (molecules) exist within a cylinder of length l, and section equal to the molecular cross section for absorption. As the time of flight of the photon is negligible compared to molecular motion, one needs only to know the probability of having no molecules in the cylinder at a given instant. This will be the probability for the photon to pass through. If the molecules are independently and randomly distributed within the cell volume $V = Sl$, the probability of having k out of N molecules in the cylinder is given by the binomial law,

$$P(k) = \frac{N!}{(N-k)!k!}\left(\frac{v}{V}\right)^k \left(1 - \frac{v}{V}\right)^{N-k} \tag{5}$$

where $v = \sigma l$ is the cylinder's volume. Then, the probability of having exactly zero particles is

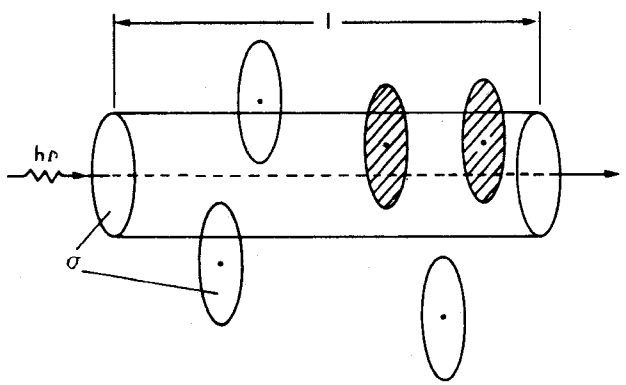
$$P(0) = \left(1 - \frac{v}{V}\right)^N \simeq e^{-\frac{Nv}{V}} \tag{6}$$

given that v/V is usually very small. This is Beer's law, as $P(0)$ is the fraction of transmitted photons, that is, the transmittance I/I_0, and Nv/V can be rewritten as $\sigma N_A C l$.

Photon Mean Path

A quantity of some interest in concentrated samples is the photon mean path. If this quantity is much less than the cell length, then virtually all light is absorbed and none transmitted. Consider a cell of infinite thickness. The mean path is then given by

$$\bar{x} = \frac{\int_0^\infty x e^{-\sigma N_A C x}\,\mathrm{d}x}{\int_0^\infty e^{-\sigma N_A C x}\,\mathrm{d}x} = \frac{1}{\sigma N_A C} \tag{7}$$



Photon path and associated cylinder. Molecules whose centers occur within the cylinder (shown with hatched cross sections) are potential absorbers.

[1] At least 20 times after 1950, see refs. *1–20*.

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Equation 7 bears some resemblance with the molecular mean free path of an ideal gas, λ (*21*)

$$\lambda = \frac{1}{\sqrt{2}\,\sigma N_A C} \tag{8}$$

where σ is the collision cross section, πd^2, d being the molecular diameter. Note, however, the $1/\sqrt{2}$ factor, that arises from the dynamic nature of this last problem. In contrast to the photon case, now the molecules can no longer be supposed immobile in the time scale of interest, owing to their comparable speeds. Equation 7 applies only to those rare molecules whose speed is much higher than the average and for which a static picture is appropriate. For the average molecule, translational motion results in an effective concentration increased by a factor of $\sqrt{2}$.

Absorption Flattening

Why is transmittance not linear with concentration? Were the total cross section the sum of the contributions of all molecules, this would be the case. That is, of course, impossible; otherwise, for sufficiently high concentrations the total cross section would exceed the cell section S. It is easy to see why this cannot be so. As the photon is absorbed, if at least one molecule occurs along its path, it does not matter how many more are behind the first one. In this way the effective molecular cross section decreases with concentration. Writing

$$1 - \frac{I}{I_0} = \frac{\sigma' N}{S} \tag{9}$$

where σ' is the effective molecular cross section and N is the number of molecules, use of Beer's law yields

$$\sigma' = \left(1 - e^{-\frac{\sigma N}{S}}\right)\frac{S}{N} \tag{10}$$

This shows that for low N σ' equals σ, while for high N σ' tends to the limit S/N. That is, close to the limit of high N, the addition of further molecules changes nothing because they always fall in the shadow of others.

Suppose that, starting with a homogeneous solution with concentration C, small clusters of molecules spontaneously form. Each of these clusters is randomly distributed within the cell and is delimited by a cylinder whose section is s, this cylinder enclosing n randomly distributed molecules (the cluster) within it. The cylinders are all oriented with the faces parallel to the cell's front face. The question is: did the clustering process affect the absorption of light by the sample? To answer the question, a slight generalization of a previous reasoning is necessary. Each cylinder may be considered as a "molecule", with a cross section equal to s. The capture probability can now be smaller than one, as a photon may pass through without finding any molecule (Beer's law holds for the cylinder). If the escape probability is β for a single cylinder and if k cylinders occur in the photon path, the global escape probability is β^k. The probability for k cylinders to occur is given by eq 5, with $v = sl$ and N replaced by N/n. Summing up all probabilities,

$$\sum_{k=0}^{N/n} P(k)\beta^k = \left[1 - (1-\beta)\frac{v}{V}\right]^{N/n} \simeq e^{-(1-\beta)\frac{v}{V}\frac{N}{n}} \tag{11}$$

or

$$\frac{I}{I_0} = e^{-(1-\beta)\frac{s}{n}N_A C l} \tag{12}$$

Since Beer's law holds for every cylinder,

$$\beta = e^{-\frac{\sigma n}{s}} \tag{13}$$

hence the effective cross section of eq 12 is

$$\sigma' = (1 - e^{-\frac{\sigma n}{s}})\frac{s}{n} \tag{14}$$

For low n, σ' reduces to σ. But for high n, σ' equals s/n and becomes independent of σ, compare eq 10. This is the phenomenon of absorption flattening, first identified by Duysens (*23*).

It occurs in dispersions of biological cells, colloids, etc. The concentration of chromophores in small volumes tends to flatten the absorption: Large cross sections "saturate" at lower macroscopic concentrations than small cross sections, as eq 14 shows. This effect should not, of course, be confused with true molecular aggregation (i.e. collective absorption) or spectral distortions arising from light scattering.

Beer's-Type Laws

Scattering processes also obey a Beer's-type law under certain conditions. In fact, if only single scattering occurs, the above derivation applies, provided a scattering cross section is defined. Light scattering by dilute suspensions (*24*), and molecular (*25*) and electron (*26*) beam scattering by gaseous samples do follow an exponential decrease with thickness and concentration.

Limitations of the Corpuscular Model

Essential to the derivation given is the concept of the photon as a pointlike particle, an idea put forward by the American chemist G. N. Lewis (who also proposed the very name photon (*27*)). While this is a convenient model for some purposes (including ours), it is by no means the whole story (*28*). In connection with this, it is important to estimate orders of magnitude for the absorption cross sections (*29, 30*). For an intense molecular transition in the visible or ultraviolet region of the spectrum, a peak absorptivity of $\epsilon \approx 10^5 M^{-1}\,cm^{-1}$ is typical. This leads to a molecular cross section $\sigma \approx 4$ Å^2, indeed close to chromophore dimensions. Braude (*31*) performed some interesting and detailed calculations in this regard. But the point should not be pushed too far. For instance, the theoretical peak cross section for a fully allowed atomic electronic transition is $\sigma_{max} \approx \lambda^2/2$, where λ is the wavelength (*32*). Clearly, this is much larger than the atomic size and suggests instead the picture of the photon as a fuzzy ball of radius $\sim\lambda$ (*32*). The absorbing species cross section σ would then be just $p\sigma_{max}$, p being the probability of absorption once the fuzzy ball encounters the chromophore. This picture also leads to Beer's law if one makes the additional assumption that absorption always proceeds sequentially, even when two or more absorbing species become momentarily enclosed within the same ball, this being a frequent occurrence for the usual concentrations in solution. For aggregates that are small compared with the wavelength, the fuzzy ball picture leads to eq 14 again, but with s replaced with σ_{max}. Negligible flattening is therefore generally predicted. For aggregates that are large compared with the wavelength, both pictures yield identical results.

The light absorption picture considered is also not valid for high intensities of radiation, where multiphoton processes become important (*33*). For two-photon absorption, for instance, light absorption follows an hyperbolic dependence with concentration (*34*).

Conclusions

A corpuscular derivation of Beer's law was given. This derivation dispenses calculus and continuum assumptions and focuses the attention on the whole cell, rather than in an "infinitesimal" slab. Absorption flattening effects were shown to be easily explained in the light of this derivation. The connection it allows with gas kinetic theory and other scattering processes is also of pedagogical interest.

For simplicity, it was assumed that all molecules had the same cross section. This is not strictly correct, however, as molecular orientation with respect to photon polarization determines also the absorption probability. It is not difficult to generalize the derivation in this regard. The same applies to mixtures of different absorbing species.

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