Terms Employed

Radiant Power, \( P \)

Synonym: I for Intensity

Transmittance

\[ T = \frac{d}{P_0} \]

Synonym: Transmission, \( T \)

Percent Transmittance:

\[
\text{with}
\]

- Path Length \( \langle b \rangle \)
- Concentration of solute: \( \langle c \rangle \)
- Absorptivity: \( \langle a \rangle \)

Molar absorptivity: \( \langle a \rangle \), if \( c \) is expressed in molarity.

The following derivation is based on the model of the absorption (shown in the figure at the right) of radiant power by the species in solution.

One says that the differential decrease \( -dP \) of radiant power for a passage through a differential distance \( dx \) is directly proportional to the concentration of the absorbing species and to the magnitude of the power available for absorption. This model then sets the stage for the derivation of the quantity Absorbance, \( A \):

\[ -dP = k \cdot c \cdot P \cdot dx \]

where

- \( k \) is said to be a function of the molecular identity of the absorbing species, a bit of a "catch-all" parameter.
- \( c \) is the concentration,
- \( P \) is the instantaneous power and
- \( dx \) is the differential change of distance in the direction of power absorption.

Dividing both sides by \( P \), we obtain

\[ \frac{dP}{P} = k \cdot c \cdot dx \]
the definite integral of which yields

\[\int \end{equation}

The details of the derivation will be exemplified in class, but suffice it to say here that the evaluation of the indefinite integral requires the assumption that when \( x = 0 \), \( P = P_0 \) and when

- \( x = \) some defined value \( b \),
- \( P_0 \) has diminished to some smaller value \( P \).

A logarithm changes sign when its argument is inverted, so effecting this change and a slight rearrangement gives us

\[
\log_{10} \frac{P_0}{P} = k \frac{b}{c}
\]

In the early days of spectrophotometers, the fraction of radiant power \( P/P_0 \) getting through a particular optical cell was easy to measure simply as the ratio of the final intensity compared to the initial intensity. Hand calculators which produce instantaneous values of natural logarithms were not yet even a dream but people did have books of logarithms to the base 10 to which they referred often when making calculations. Thus the equation above for them was more convenient if converted to the following form

\[
A = \log_{10} \frac{P_0}{P} = a \ b \ c
\]

The value of \( k \) is dependent upon the units of \( b \) and \( c \). In the most general final result of this derivation we allow \( k/2.303 \) to equal the absorptivity, \( a \), so that the equation becomes

\[
[A = \log_{10} \frac{P_0}{P} = a \ b \ c]
\]

In the case that concentration is measured in molarity, we call "a" the \textit{molar absorptivity} and give it the symbol epsilon, or , so that the equation takes the form

This equation is called \textit{Beer's Law} for the investigator who first recognized the simple relationship between the logarithm of the ratio of \( P_0 \) and \( P \) and the concentration.
Beer's Law also applies to mixtures of non-interacting species

which says that if individual solutions of substances 1, 2 and 3, having concentrations $c_1$, $c_2$ and $c_3$ produce, at the same wavelength, absorbances $A_1$, $A_2$ and $A_3$, respectively, the total absorbance of a single solution of substances 1, 2 and 3, having concentrations $c_1$, $c_2$ and $c_3$ in that solution would produce, at the same wavelength, an absorbance

$$[A_{TOTAL} = A_1 + A_2 + A_3]$$

This prediction has been verified experimentally.

Limitations on Beer's Law

Some deviations in linearity are connected with changes in absorptivity with wavelength and the specificity of the instrument in being able to isolate the smallest increment of absorbing wavelengths. Others are a function of the absorbing molecules and their interactions in solution. In the first case, if the increment of wavelengths measured by the instrument is small and the molar absorptivity of the species being observed is near the maximum then any change in the molar absorptivity in this region is small and Beer's Law is obeyed. If, however, species are being observed in a region where there is a noticeable gradient in the molar absorptivity and the increment of wavelengths is large, second- and higher order relationships between absorbance and concentration begin to be observed, that is non-linear perturbations in Beer's Law are observed. In the second case, as concentration of the species being observed increases there is a greater probability in interactions between the absorbing molecules, and a change (usually downward) in the absorbance. Any interaction likely interferes with the electronic band structure in the absorbing species and and energy absorption levels change with a resulting exhibition of a non-linear perturbation of Beer's Law.

For these reasons, dilute solutions are used and the absorbance is measured at a wavelength referred to as $\lambda_{max}$. $\lambda_{max}$ is
found by plotting absorbance vs. wavelength, as shown in the diagram of the absorbance of the iron-bipyridyl complex at right. (Thanks to Ms. Khanh Nguyen for sharing her experimental plot with us)

Note that at $\lambda_{\text{max}}$ there is no gradient in absorbance with wavelength. A change in absorbance is negligible over any reasonably small increment of wavelength.

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**A brief Journey into the Theory of Absorbance**

The model which helps us to explain absorbance is based on quantized energy states observed in molecular species. These states come in three forms: electronic, vibrational and rotational. A photon of sufficient energy can interact with a molecule to "bump" it into a higher energy level or energy state. Specialists in the field speak of electronic, vibrational and rotational energy **levels** but one also hears the terms **vibrational modes** and **rotational modes**. These terms help specialists in the field to explain the complexity of observed spectra. Molecular energy transitions extend from the microwave at the low energy end of the electromagnetic spectrum to the ultraviolet at the higher energy end. In very broad terms, electronic energy transitions are effected by photons whose energies are characteristic of the visible and ultraviolet parts of the spectrum, vibrational changes by infrared and purely rotational changes occur by photons whose energies lie in the microwave region of the spectrum.

The model says that absorption of electromagnetic energy comes about if a photon of an energy sufficiently close to an allowed energy transition (electronic, vibrational or rotational) of a molecule, $M$, passes sufficiently close to a molecule or ion to bring about a change in the wave equation to a higher energy level. Absorbance of this energy results in an excited state, $M^\ast$. The excited state then emits subsequent photons dropping down to intermediate energy levels. The standard equation which describes this action is

$$h = \frac{\lambda \cdot c}{\lambda'}$$

When one considers that the organization of life depends on the input of energy to give rise to higher organization followed by subsequent emission of energy in smaller units but often coupled to reactions needing the smaller units of energy, as the manifestations of higher organization change shape, composition and whose energy spontaneously drops to lower energy states, the equation above may have implications more far reaching and profound than that which will be covered here.

Each step indicated above, after the initial input of $h$, depends on the release of energy caused by events within the excited molecule and are not well understood. We say simply that there is some characteristic time, a half-life, during which half of the excited molecules at some level decay to a lower level. The model used for this is the same as that applied to spontaneous radioactive decay. In the case of molecules which have been raised to excited energy states, the half life characteristically varies between a billionth of a second and ten billionths of a second.

The deep red-violet color of the MnO$_4^-$ ion is caused by the absorbance of energy in the green region of the visible spectrum. The model used to describe the mechanism of the energy absorbance is that of transitions of energy levels of delocalized electrons involved in the bonding of the Mn atom in the complex ion. This is an electronic energy transition.
Gaseous HCl absorbs energy characteristic of the energy levels produced by resonance states of its covalent bond which in turn is related to the force constant of the bond and the mass of each atom. The model applied in this case is that of a vibrating spring (harmonic oscillator). The differences in those resonance states fall in the far infrared region of the electromagnet spectrum.

Water molecules in the gaseous state are free to rotate around any of three orthogonal axes. That such molecules can absorb energy consistent with a rigid rotor model given allowed energy levels suggests a phenomenon similar to that of electronic and vibrational energy transitions. Water in the liquid state suffers continuous intermolecular interactions owing to the close proximity of other water molecules. The allowed energy levels are said to be somewhat "fuzzed out" allowing energy absorbance within whole bands of energy in the microwave region of the spectrum. The microwave oven takes advantage of such a band structure. The frequency of a microwave oven is 2.45 GHz, and, as it turns out, NOT exactly centered on a resonant frequency for the water molecule. Had a resonant frequency been selected, most of the radiation would be absorbed by water molecules at the surface and the interior of the food would remain cold. Lower frequencies would penetrate better but not cook as well. Higher frequencies would not penetrate as well. 2.45 Ghz was chosen because of non-interference with assigned electromagnetic spectrum assignments for communication, convenience in implementation and reasonable penetration of the microwave energy into the food.

The absorbance spectrum of water is illustrated here with the x-axis scaled in a logarithmic fashion in order to include a huge range of frequencies. So as better to orient you to the "real-world" uses of the spectrum, the image shows a frequency range starting around the amplitude modulation (AM) radio transmission band and progressing through the FM band, microwave, infrared, visible and ultraviolet regions of the spectrum. Note that at the frequencies shown here below $10^{-3}$ gigahertz, water is a reasonably transparent liquid. Electromagnetic radiation in that portion of the spectrum is not absorbed. There is increasing absorption as the frequency of radiation progresses through the microwave and IR regions. That is to say, water becomes an opaque liquid. Then it becomes transparent in the visible region and goes opaque once again in the ultraviolet region.

The table below gives an example for each of the energy transitions described above.

<table>
<thead>
<tr>
<th>Molecule/ species</th>
<th>Formula</th>
<th>Absorbing wavelength</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>MnO$_4^-$</td>
<td>500 nm</td>
<td>600,000 GHz</td>
</tr>
<tr>
<td>Molecule/ species</td>
<td>Formula</td>
<td>Absorbing wavelength</td>
<td>Frequency</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>HCl</td>
<td>~0.04 cm</td>
<td>750 GHz</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>~12 cm</td>
<td>2.45 GHz</td>
</tr>
</tbody>
</table>

Every molecular species has its own characteristic absorption frequencies but the rule that electronic transitions occur in the visible and ultraviolet, vibrational transitions in the infrared and rotational transitions in the microwave regions of the electromagnetic spectrum is generally followed.

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