

Hello students, I am Miss Shreya Avdhoot Silimkhan

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The title of the unit is UV visible

spectroscopy and the name of the

module is derivation of Beer-Lambert's law and deviations from Beers law.

So I will be discussing statement

of Beer Lambert's law, derivation of

Beer-Lambert's Law and the validity and

deviations from Beer-Lambert's law.

So upon going through this module,

the students will be able to

state the Beer-Lambert's law,

derive the Beer-Lambert's law,

understand the validity of Beer-Lambert's

law, and know the limitations of Beers law.

So coming to Beer-Lambert's law,

a combination of Lambert's law and Beers law,

it results in the Beer-Lambert's law.

So these are two separate laws,

Students, Beers law and Lambert's law when combined together,

gives us the Beer-Lambert's law.

It governs the absorption of light by
absorbing media, such as solutions.

So let us see the statement
for Beer-Lambert's law.

It states that the fraction of incident
radiation absorbed is proportional to the
number of absorbing molecules in its path.

To tell you,

in a mathematical form,

A is equal to $\epsilon C l$.

So first I will like to start with

Lambert's law transmission of light.

So we are coming to the derivation.

So here is a statement for Lambert's

Law. When a monochromatic light is passed

through a pure homogeneous medium,

the decrease in the intensity of light

with thickness of the absorbing medium

at any point X is proportional to

the intensity of the incident light.

So to write it in an equation form minus

dI by dx is directly proportional to I ,
so further minus dI by dx is equal to $-K I$.

dI is the small decrease in intensity
of the light passing through a small
thickness dx . K is the constant
of proportionality called the
absorption coefficient.

So our first equation is minus dI by dx
is equal to $-K I$.

The intensity I at any point
 X at a distance x .

OK here, there are two alphabets.

Distance is denoted by the small letter x .

So the intensity I at any point capital
letter X at a distance x from the start
of the medium can be found in terms of
the original intensity given by I_0 .

So equation one,

we can rewrite it as dI upon

I is equal to minus $-K dx$,

you have to label this as equation 2.

when X is equal to 0 then I is equal to.

10. Integrating equation 2

between the limits.

Now we are integrating from limits X is

equal to 0 to X and I is equal to I_0 to

1. We get this equation.

Integral going from I to I_0

I / I_0 is equal to integral x

going from zero to x minus Cdx .

Then we integrate equation

2 between the limits.

X is equal to 0 to X and I

is equal to 0 to I .

So then we obtain equation 3. \ln of I / I_0

is equal to minus kx .

Further, we simplify it and write

it as I / I_0 is equal to e^{-kx}

and equation 4,

We get it as $I = I_0 \times e^{-kx}$

so this equation it expresses how

the original intensity I_0 is

reduced to intensity I after passing
through a thickness x of the medium.

Then further we take equation

3 and we write it as

$$2.33 \log I/I_0 = -kx$$

$$\log I/I_0 = -kx/2.303.$$

so equation 5 will be obtained as

$$\log I/I_0 = -k'x$$

Equation 6 we will obtain it as

$$I = I_0 10^{-k'x} \text{ this is your equation}$$

6 where k' has the value of

$$k' \text{ is } k / 2.303.$$

It is called as the extinction

coefficient of the substance,

which is the absorbing medium.

This quantity is referred to

as absorption coefficient or

absorptivity of the substance

$-\log I/I_0$ is called.

Absorbance of the medium.

Next we come to Beers law. Students

let us see the statement.

This law states that when a monochromatic

light is passed through a solution,

the decrease in the intensity of

light with the thickness of the

solution is directly proportional

not only to the intensity of the

incident light but also to the

concentration C of the solution.

Coming to the derivation,

we write an equation.

$-dI/dx$ is directly proportional to I

$\times c$ this is your equation 1.

Next $-dI/dx = \epsilon I c$.

Epsilon is a constant of

proportionality and is called

molar absorption coefficient.

Its value depends upon the nature

of the absorbing solute and the

wavelength of the light which is used.

Then we again. Write

$$dI/I = -\epsilon c dx$$

then again like how we did for Lambert's law

again we integrate the equation

between the limits X is equal to 0

to X and I is equal to a zero to I.

So upon integrating we obtain

$$\text{equation 2. } \ln I/I_0 = -\epsilon c dx$$

Then equation 3 you will obtain

$$\text{it as } I/I_0 = e^{-\epsilon c x}$$

$$\text{And equation 4 is } I = I_0 e^{-\epsilon c x}$$

This equation expresses how the

intensity of a monochromatic light

falls from I_0 to I on passing

through a thickness x of a solution

of concentration C.

$$2.33 \log I/I_0 = -\epsilon c x$$

Next we simplify it

$$\log I/I_0 = -\epsilon c x / 2.303$$

This is equation 5

$$\log I/I_0 = -\epsilon' c x$$

$$\epsilon' = \epsilon / 2.303$$

Earlier this was referred to
as molar extinction coefficient
of the absorbing solution.

But now this quantity is called
molar absorption coefficient or you
can call it as molar absorptivity
of the absorbing solution.

So here I have put up a diagram showing
a cuvette and you can see the incident light.

It is referred to as I_0 and
upon passing through the cuvette,
through the solution it is referred to as I .

And you can also see the length of
the cuvette and c refers to the
solution which you have placed in the cuvette.

C is the concentration
of the solution in the cuvette.

Coming to deviations from Beers law.

The linear relationship between optical
density and concentration of solution
is not observed at concentrations above 10^{-2} molar.

Hence concentrated solutions do not obey Beer-Lambert's equation.

The law is not obeyed if the absorbing species reacts with the solvent, dissociates or associates in the solution.

The molecules of the absorbing species. They should remain as simple molecules and they should not undergo any kind of change in the molecular condition.

And temperature fluctuations and entry of stray light into the absorbing system can also lead to deviations from Beer-Lambert's law.

The light incident,

This is the most important point.

The light incident on the absorbing medium should be monochromatic, otherwise minor deviations from Beer-Lambert law are observed.

This is why monochromators have to be used to produce monochromatic beams.

The molar extinction coefficient.

It depends on the refractive index of the absorbing medium.

At high concentrations this changes are considerable,

but at concentrations below 10^{-2} molar,

this changes can be neglected.

When Beer-Lambert law is obeyed, the calibration plot will be obtained as a straight line passing through the origin.

If there are deviations from Beer-Lambert's law, the calibration plot will curve either.

Upward, meaning it will be known as a positive deviation,

and if the calibration plot curves downward, it will be known as a negative deviation.

So here I have put up two diagrams showing the calibration plot,

absorbance versus concentration,
and on the left hand side you can
see a calibration line showing the
relationship between absorbance and
concentration on the right hand side.

You can see the deviations.

Positive deviation is if the plot is pointing upward and negative
is when the plot is pointing downward.

So coming to validity of Beer-Lambert's law.

This law is strictly applicable
to dilute solutions and the
concentrations of the solution.

They have to be below 10^{-2} molar,

so such solutions they obey the

equation. Optical density or you

can call it as absorbance is

equal to minus log to the base.

10 of T is equal to epsilon,

Cl. According to this equation,

the optical density is proportional

to the concentration of the solution

and transmittance is inversely
proportional to the concentration.

So coming to the summary of this module,
a combination of Lambert law with the Beers,
law results in the Beer-Lambert's law.

So this law states that fraction
of incident radiation absorbed
is proportional to the number of
absorbing molecules in its path.

A is equal to $\epsilon \cdot C \cdot L$.

Concentrated solutions do not
obey Beer-Lambert equation.

And when Beer-Lambert law is obeyed,
the calibration plot will be obtained
as a straight line passing through the
origin and the last point is the Beer-Lambert's
law is strictly applicable to dilute.

Solutions whose concentrations are
below 10^{-2} molar,

So this are the references Thank
you so much for listening.