Shree H.N.Shukla College of Science Rajkot
B.Sc. (Sem- 5) (CBCS)
CHEMISTRY: [503]

Colorimetry

Unit – 3

❖ Content:

1. Introduction
2. Grotthus Draper law,
3. Lambert's law,
4. Beer's law,
5. Lambert's-beer's law and Derivation, application & deviation of Lambert's law
6. Spectrophotometric titration with graph and proper explanation
7. Deficit of absorbance by product and titrant
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10. Deficit of absorbance by product only

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Photochemistry: **Photochemistry** is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm)

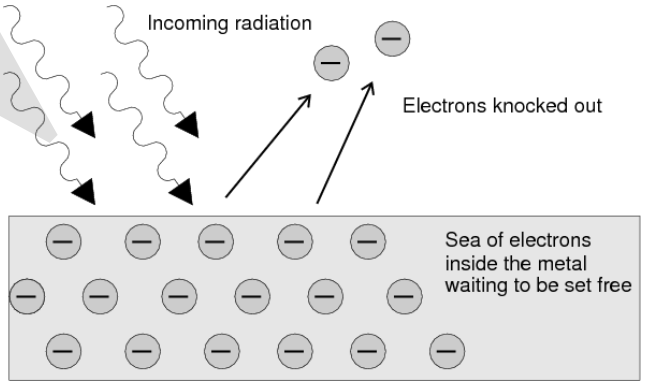
The reactions which can be brought about by light radiations are called photochemical reactions.

Photochemical Reaction	Thermal Reaction
These reactions involve absorption of light radiations.	**These reactions involve absorption or evolution of heat energy.**
Presence of light is the primary requirement.	**These reactions can take place in light as well as in dark.**
Temperature has very small effect.	**Temperature has significant effect.**
ΔG may be +ve or –ve.	**ΔG is always –ve.**
Photochemical activation is highly selective process.	**Thermal activation is not selective in nature.**

❖ Law of photochemistry:

1. **Grotthus Draper Law**:- "Only those radiations which are absorbed by a reacting substance or system are responsible for producing chemical change."

- According to this law, all light radiations are not bringing the chemical reaction. Some are increase the kinetic energy of molecule while some are re-emitted. (i.e. fluorescence)
- When a monochromatic or heterogeneous light (I_o), is incident upon a homogeneous medium, a part of it is **absorbed (I_a)**, a part is **reflected(I_r)** and remaining is **transmitted (I_t)**.



It means that,

$\mathbf{I_o = I_r + I_a + I_t}$

Where, I_o = Intensity of incident light

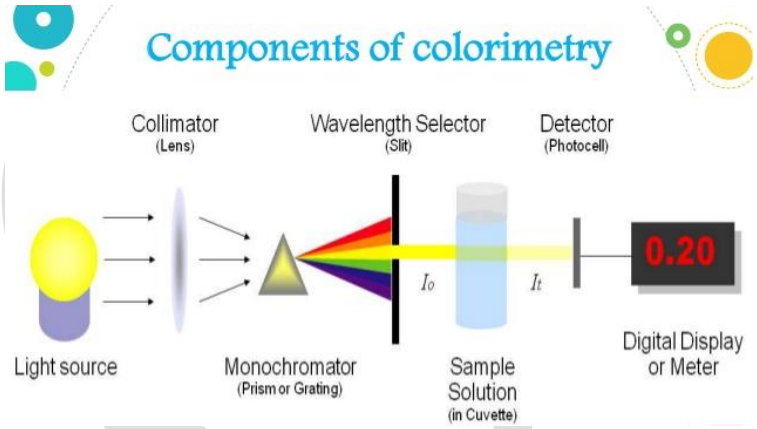
I_a = Intensity of absorbed light

I_r = Intensity of reflected light

I_t = Intensity of transmitted light

- However, the absorbed radiation does not necessarily cause a chemical reaction. The above phenomenon may be made clearer as follows.
- Since light is a form of energy, so the absorption of light means absorption of energy. Hence, the primary effect in all photo process is,
  1. Either an increase in thermal energy of a system or
  2. To raise the electron's in atoms or molecules of the system to higher energy levels. This process is called **Activation**.

❖ Lambert's Law:



- A relationship between the intensity of absorbed light (I_a) and transmitted light (I_t) has been given by Lambert in 1760 and extended by Beer in 1852.
- When a monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation.

Or

The rate of decreament of intensity with the thickness of absorbing medium is proportional to the intensity of the penetrating radiations.

$dI \propto Idt$

$dI = -KIdt$ (-ve sign due to intensity of light is decreased) .....(1)

$\frac{dI}{I} = -Kdt$

Where, I = Intensity of light
t = The thickness of absorbing medium
k = absorption or extinction coefficient

Equation (1) can be expressed as,

$+\frac{dI}{I} = -K.dt$ .....(2)

Integration of equation (2) ,

$\int \frac{dI}{I} = -K\int dt$ .....(3)

$\ln I_t = -kt + C$ .....(4)

When t = 0, $I_t = I_o$

$\therefore C = \ln I_o$

$\ln I_t = -kt + \ln I_o$

$\therefore \ln I_t - \ln I_o = -kt$

$\therefore \ln I_t / I_o = -kt$ ……(5)

$\therefore$ **$I_t = I_o\ e^{-kt}$** .....(6)

Where, k = absorption coefficient

I_t = Intensity of transmitted light

I_o =Intensity of incident light

Equation (6) is the mathematical expression of $T = \frac{I}{I_0}$ Lambert's law.

Transmittance or Transmission :

Transmittance (T) is the fraction of incident light which is transmitted.

It can be expressed mathematically as follows.

Where, I = Transmitted light

I_o= Incident light

Absorbance / Optical Density:

It is the common logarithm of the ratio of incident to transmitted spectral radiant power through a material.

$A = Log_{10} (I_0/I) = 1/ T$

Where, I_0 = intensity of the incident light

I = intensity of that light after it passed through the sample

Beer's law:

- This law states that when an absorbing medium is in gaseous state or dissolved in transparent solvent; the absorption coefficient K is proportional to the co0ncentration C.

$K \propto C$ ….(1)

$\therefore K = eC$

Where, C = Concentration & e = new constant

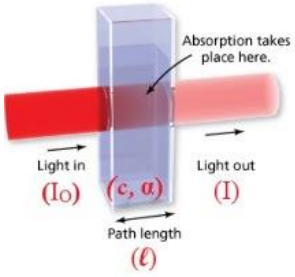
Substitute equation (1) in $I_t = I_o.e^{-kt}$

$\therefore I_t = I_o.e^{-ect}$ ....(2)

This is mathematical expression of **Beer-Lambert's law.**

From equation (2)

$\ln \frac{I_o}{I_t} = ect$ ....(3)



$$A = log_{10}(\frac{I_o}{I}) = \varepsilon cl$$

$$A = \varepsilon cl$$

- The value of 'e' is dependent on the concentration unit of the substance. If the value of 'C' is in mole/litre and thickness 't' is in cm than 'e' is known as **molar extinction co-efficient** or **molar absorption coefficient**.
- The relation of absorption A ,transmittance T and molar absorption coefficient e can also be expressed as

  $\mathbf{A = ect = \ln \frac{I0}{It} = \ln \frac{1}{T} = - \ln T}$

  A = ϵ**ct** (small e is also expressed by ϵ (epsilon) in above case.

Note:

Molar absorptivity / Specific absorption: Absorbance of the solution with 1 cm thickness and mole/decimeter concentration is specific absorption or molar absorptivity**.**

Questions (1 Marks):

Question	Answer
1. Give the mathematical expression of Lambert-Beer law.	A = ect = $\ln \frac{I0}{It}$
2. **A = ect = ln** $\frac{I0}{It}$ **= ln** $\frac{1}{T}$ **= _____**	-ln T
3. Lambert's law is expressed in mathematical form	$+\frac{dI}{I}$ = -K.dt
4. Law of photochemistry was proposed by____	T. Grotthus
5. The wave length range of photo chemical reaction lies between_____	2000 – 8000 Å

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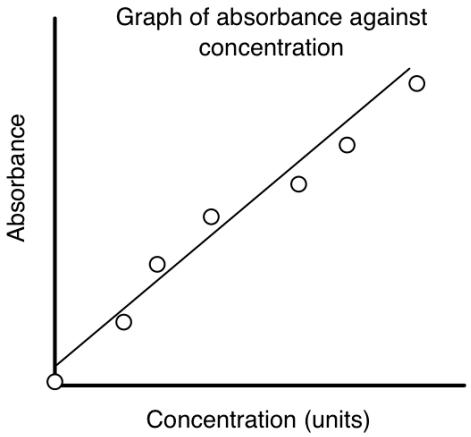
❖ **When it said that Lambert-Beer law is followed?**

For a series of solution of different concentration when irradiated by the radiation and its absorbance A or optical density (O.D.) and transmittance is measured by spectrometer or colorimeter then by plotting the graph A→ C is straight line than is said that Lambert-Beer's law is followed.



❖ **Deviation from Lambert-Beer's law:**

1. Form of the color solution should not be changed, otherwise it will show deviation.
2. Ionization, decomposition or combination should not be done in colored solution otherwise it shows deviation
3. Only dilute solution follow Lambert-Beer's law. Concentrated solution do not follow the law.
4. Dispersed particles should not be present in the solution because dispersed particle can dispersed the incident rays which cause deviation from the law.
5. Only desired frequency or wave length of the light should be completely transparent and of true color.
6. Solution should be completely transparent and of true color.
7. Color of the solution should not change even after a long time.

❖ **Spectrophotometric estimation:**

It consists of two main components.

1. Photoelectric colorimeter
2. Spectrometer

- Ray of different wavelength can be obtained by spectrometer with the use of granting or prism band with 5 nm width can be obtained. Ray of UV or visible region is possible to be obtained.
- Endpoint is decided from the value of the absorbance by solution in Spectrophotometric estimation. When monochromatic light is allowed to pass through the solution at that time Beer's law is applicable.

  $\mathbf{A = ect = ln \frac{I0}{It}}$

  If e and t are constant than, A = C

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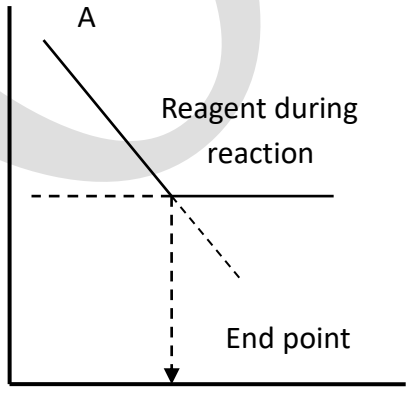
Here, I_o = Intensity of incident radiation
I_t = Intensity of transmitted radiation
$\in$ = molar absorbance coefficient
C = Concentration of the solution
t = thickness of the solution

- When the light intensity is constant than absorbance is proportional to the concentration of solution. In such estimation reactant or product can absorb only definite wavelength of light.
- The graph is plotted of estimated volume against absorbance, from which endpoint can be decided. The curve depends upon the optical characteristics of estimator and product. It is more dependent on the wavelength of the light.

Type 1: **Lacking of absorbance by reaction product and estimating reagent.**

When product and estimating reagent have non-absorbing characteristics and only reactant can absorb radiation at that time this graph is possible.

- Initially concentration of reactant is found more With the progress of the reaction concentration of the reactant decreases and hence absorbance value decreases. At the end point absorbance becomes minimum.
- Then by adding more estimating reagent which has non-absorbing characteristics, absorbance remains constant. Endpoint is obtained at the point at which two lines intersect each other.

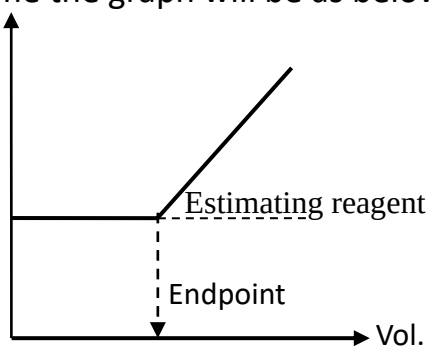


Type 2 : Lacking of absorption of radiation by reactant and product.

When reactant and product show non-absorbing (lack of absorption), characteristics and only estimating reagent absorb radiation at that time the graph will be as below.

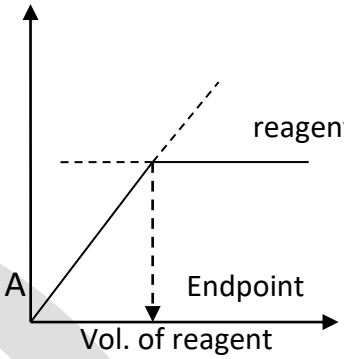
- Initially the conc. Of reactant is found maxima but reactants do not show absorbance value obtained initially will be minimum.

With the addition of reagent reaction between reactants and estimating reagent will start and product will be obtained.



- In this case, product does not show absorbance hence absorbance will b e constant until the completion of reaction.
- After completion with further addition of estimating reagent value of A increase as reagent absorbs the radiation. Intersect of two lines show endpoint.

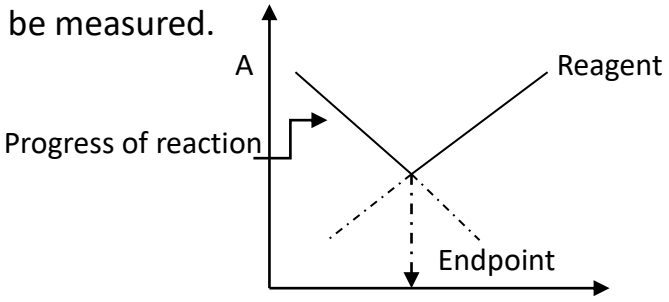
Type 3 : Lacking of absorbance by reactant and products



- When reactant and reagent are colored and product is colorless and product does not show absorbance than above type of graph is obtained.
- Initially conc. of reactant is maximum , hence value of A is maximum. With the addition of reagent, reactant and reagent reacts to form product.
- Thus, conc. of reactant absorbance value are decreasing. Absorbance value becomes minimum at the end point.
- Later on with the addition of more reagent value of A increase. Although in photo-metric estimations, absorbance is related to conc. slight deviation in the graph is observed and a curve instead of straight line is obtained. Hence, by extra plotting both the curves endpoint can be measured.

Type 4: Lacking of absorbance by reaction product

When reactant and reagent are colored and product is colorless and product does not show absorbance than above type of graph is obtained.
Initially conc. of reactant is max., hence value of A is max. With the addition of reagent, reactant and reagent reacts to form product.
Thus, conc. of product increase but product does not absorb and hence with the decrease in conc. of reactant absorbance value are decreasing. Absorbance value becomes minimum at the end point.
Later on, with the addition of more reagent value of A increases. Although in photometric estimations, absorbance is related to conc. slight deviation in the graph is observed and a curve instead of a straight line is obtained. Hence by extra plotting both the curves endpoint can be measured.



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Questions: (MCQ)

1. **Beer Lambert's law gives the relation between which of the following?**
a)Reflected radiation and concentration
b)Scattered radiation and concentration
c) Energy absorption and concentration
d) Energy absorption and reflected radiation

2. **In which of the following ways, absorption is related to transmittance?**
a) Absorption is the logarithm of transmittance
b) Absorption is the reciprocal of transmittance
c) Absorption is the negative logarithm of transmittance
d) Absorption is a multiple of transmittance

3. **Which of the following is not a limitation of Beer Lambert's law, which gives the relation between absorption, thickness, and concentration?**
a) Concentration must be lower
b) Radiation must have higher bandwidth
c) Radiation source must be monochromatic
d) Does not consider factors other than thickness and concentration that affect absorbance

4. **Beer's law states that the intensity of light decreases with respect to _____**
a) Concentration b) Distance c) Composition d) Volume

5. **Lambert's law states that the intensity of light decreases with respect to _____**
a) Concentration **b) Distance** c) Composition d) Volume

6. **The representation of Beer Lambert's law is given as A = abc. If 'b' represents distance, 'c' represents concentration and 'A' represents absorption, what does 'a' represent?**
a) Intensity b) Transmittance **c) Absorptivity** d) Admittance

7. **Which of the following is not true about Absorption spectroscopy?**
a) It involves transmission
b) Scattering is kept minimum
c) Reflection is kept maximum
d) Intensity of radiation leaving the substance is an indication of concentration

8. **Transmittance is given as $T = P/P_o$. If P_o is the power incident on the sample, what does P represent?**
a) Radiant power transmitted by the sample b) Radiant power absorbed by the sample
c) Sum of powers absorbed and scattered d) Sum of powers transmitted and reflected

9. **What is the unit of absorbance which can be derived from Beer Lambert's law?**
a) L mol^{-1} cm^{-1} b) L gm^{-1} cm^{-1} c) Cm **d) No unit**

10. **What is the unit of molar absorptivity or absorptivity which is used to determine absorbance A in Beer Lambert's formula?**
a) L mol^{-1} cm^{-1} b) L gm^{-1} cm^{-1} c) Cm d) No unit

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