<h1 style="text-align:center">UV-Visible Spectroscopy</h1>

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UV-Visible Spectroscopy

The wavelength range of UV radiation is 200 nm- 400 nm. There are mainly two types of UV region.

1. 200 nm - 400 nm that is called near ultraviolet region.

2. Below 200 nm that is called far ultraviolet region. The wavelength of visible radiation is 400 nm- 800 nm

Wavelength in UV and visible region is expressed in nanometers or in angstroms. Absorption is expressed in terms of wave number (cm^{-1}).

Absorption spectra arise from transition of electron or electrons within a molecule from a lower electronic energy level to a higher electronic energy level. Ultraviolet emission spectra arise from the reverse types of transition. For the radiation to cause electronic excitation, it must be in the UV region of the EMR spectrum.

Radiation in this region is of sufficient energy to cause electronic transition of outer valence electrons.

Both organic and inorganic species exhibit electronic transitions in which outermost or bonding electrons are promoted to higher energy levels. Electronic transitions are associated with vibrational as well as rotational transitions.

A compound appears coloured if it selectively absorbs light in the visible region. The main function of absorbed energy is to raise the molecule from ground energy state (E_0) to higher excited energy state (E_1). The difference is given by:

$\Delta E = E_1 - E_0 = h\nu = hc/\lambda$, ΔE depends upon how tightly the electrons are bound in the bonds and accordingly, absorption will occur in UV or visible range, for example; If the electrons of a molecule are tightly bound as in compounds containing sigma bonds (e.g., saturated compounds) no light of region will be absorbed. The light of UV region will only be absorbed and hence compound appears colourless.

If the electrons of molecule are loosely bound as in unsaturated compound. Such absorption may occur in visible region and substance will appear as coloured.

Energy absorbed in the ultraviolet region produces change in the electronic energy of the molecule that is resulting from transitions of valance electrons in the molecule. There are three types of electrons in organic molecules.

a) σ (sigma) electrons- they are found in saturated systems like alkane. They require large amount of energy for their excitation and hence do not show absorption in UV region. Their absorption band is appeared in vacuum UV region. Hence, compounds containing σ- bonds do not absorb in near UV region. For example, saturated hydrocarbons are transparent in near UV region and thus they can be used as solvents.
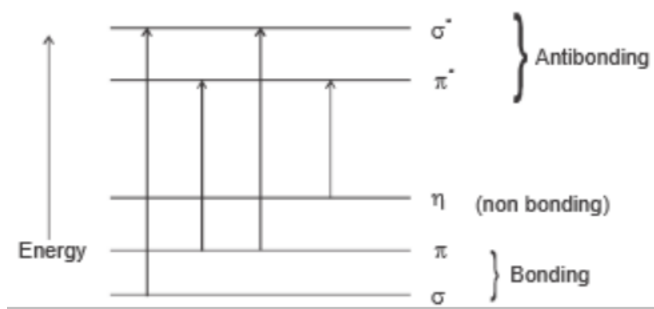
b) π(pie) electrons- they are found in multiple bonds. They are generally mobile electrons. Since π- bonds are weak bonds, the energy produced by UV radiation can excite ∏- electrons to higher energy levels.

c) n (non-bonding) electrons- valance electrons which do not participate in chemical bonding in molecule are called as non-bonding electrons or n electrons. These are located principally in atomic orbital of N, O, S and halogens(X) as a lone pair of electrons. They can be excited by UV radiation.

Principle of UV-Visible Spectroscopy: The Principle of UV-Visible Spectroscopy is based on the absorption of ultraviolet light or visible light by chemical compounds, which results in the production of distinct spectra. Spectroscopy is based on the interaction between light and matter. When the matter absorbs the light, it undergoes excitation and de-excitation, resulting in the production of a spectrum.

When matter absorbs ultraviolet radiation, the electrons present in it undergo excitation. This causes them to jump from a ground state (an energy state with a relatively small amount of energy associated with it) to an excited state (an energy state with a relatively large amount of energy associated with it). It is important to note that the difference in the energies of the ground state and the excited state of the electron is always equal to the amount of ultraviolet radiation or visible radiation absorbed by it

Laws of Absorption: The fraction of the photons absorbed by the molecule at a given frequency depends on
1. The nature of the absorbing molecules
2. The concentration of the molecules (C). The higher the molar concentration, the higher is the absorption of photons.
3. The length of the path of the radiation through the substance or the thickness of the absorbing medium. Larger the path length (in cm), larger is the number of molecules exposed and greater is the probability of photons being absorbed.
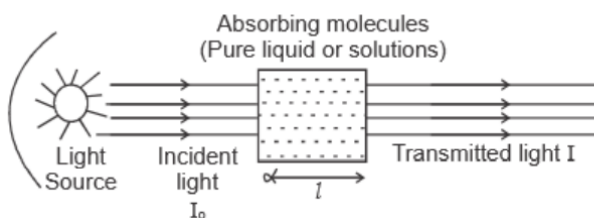
Beer's and Lambert's Law: When a light passes through absorbing medium at right angle to the plane of surface or the medium or the solution, the rate of decrease in the intensity of the transmitted light decreases exponentially as the thickness of the medium increases arithmetically.

Accordingly, Lambert's law can be stated as follows: *"When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of light."*

Mathematically, the Lambert's law may be expressed as follows.

$- dI/dl \propto I$

$-dI/dl = KI$ . . . .(1)

Where I = intensity of incident light

l = thickness of the medium

K= proportionality constant

By integration of equation (1), and putting $I=I_0$ when $l=0$,

$I_0/I = kl$ or $I= I_0 e^{-kl}$

Where, I_0 = intensity of incident light

I = intensity of transmitted light

k = constant which depends upon wavelength and absorbing medium used

By changing the above equation from natural log, we get,

$I = I_0 e^{-Kl}$ . . . .(2)

Where K = k/2.303

So, $I = I_0 e^{-0.4343\ kt}$

$I = I_0 10^{-Kl}$ . . . .(3)

Beer's law may be stated as follows: *"Intensity of incident light decreases exponentially as the concentration of absorbing medium increases arithmetically."*

The above sentence is very similar to Lambert's law. So,

$I = I_0 e^{-k'\,c}$

$I = I_0 10^{-0.4343\ k'\,c}$

$I = I_0 10^{K'\,c}$ . . . .(4)

Where k' and K'= proportionality constants

c = concentration

By combining equation (3) and (4), we get,

$I = I_0 10^{-acl}$

$I_0/I = 10^{acl}$

Where, K and K' = a or ε

c = concentration

l or b = thickness of the medium

$\log I_0/I = \varepsilon lc$ . . . .(5)

Where ε = absorptivity, a constant dependent upon the λ of the incident radiation and nature of absorbing material. The value of ε will depend upon the method of expression of concentration.

The ratio I_0/I is termed as transmittance T, and the ratio $\log I_0/I_t$ is termed as absorbance A. formerly, absorbance was termed as optical density D or extinction coefficient E. the ratio

I_0/I is termed as opacity. Thus, $A = \log I_0/I$ . . . .(6)

From equation (5) and (6),

$A = \varepsilon lc$ . . . .(7)

Thus, absorbance is the product of absorptivity, optical path length and the concentration of the solution. The term $E^{1\%}_{1cm}$ or $A^{1\%}_{1cm}$ refers to the to the absorbance of 1 cm layer of the solution whose concentration is 1 % at a specified λ.

According to equation (7),

$A = \log I_0/I$ Transmittance T is a ratio of intensity of transmitted light to that of the incident light.

$T = I_0/I$

The more general equation can be written as follows:

$A = \log I_0/I = \log 1/ T = - \log T = alc = \varepsilon lc$ …..(8)

Thus, absorbance A, also known as **optical density**, is directly proportional to (i) the concentration c of the absorbing species and (ii) the path length l and has no units. Eq. (8) is the mathematical expression for Lambert's Beer law.

ε is defined as the absorbance of the solution of unit molar concentration (1M) placed in a cell of path length one cm. If c is expressed in mol dm^{-3}, then the unit for ε is $dm^3\ mol^{-1}\ cm^{-1}$.

Limitations of Beer –Lambert's: law Beer-Lambert's law is strictly valid only in dilute solutions. For dilute solutions, a linear relationship is exhibited by a plot of absorbance (A) as a function of concentration of the absorbing substance (c), as shown in Fig 3.2.
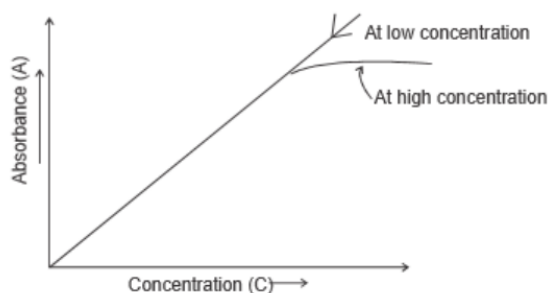

Fig 3.2 Plot of Absorbance versus Concentration

(i) Real deviations occur at higher concentration of the absorbing species. At higher concentrations (>10-3M), there is a change in the refractive index of the solution.

(ii) (ii) Chemical deviations occur when there is more than one absorbing species present in the solution. When the absorbing molecules associate or dissociate in the solution, there is a change in the number of absorbing species.

(iii) (iii)Instrumental deviation occurs due to changes in absorptivity of the species as a function of instrumental bandwidth.

Transmittance T Transmittance is defined as the "fraction of the incident light that is transmitted by a given species".

$T = \frac{I}{I_0}$ where I is the intensity of transmitted light and I_0 is the intensity of incident light.

(Absorbance) A = εcl

$log \frac{I_0}{I} = εcl$

A = - logT

A = log = εcl …..(9)

Transmittance T is expressed as % T.

2. Quantitative analysis: Many organic compounds and inorganic complexes may be determined by direct absorbance measurement values using the Lambert's Beer law.

A = εcl

A plot of Absorbance (A) vs. c the concentration gives a linear plot.

3. Determination of dissociation constants of weak acids and bases from the change in absorption spectra with pH.

4. Study of kinetics of chemical reactions.

5. Study of electronic structure of molecules such as vitamins, detecting steric hindrance, etc.

INSTRUMENTATION:

Instruments for measuring the absorption of U.V. or visible radiation are made up of the following components;

1. Sources (UV and visible)
2. filter or monochromator
3. Sample containers or sample cells
4. Detector

1. Radiation source: It is important that the power of the radiation source does not change abruptly over its wavelength range.

The electrical excitation of deuterium or hydrogen at low pressure produces a continuous UV spectrum. The mechanism for this involves formation of an excited molecular species, which breaks up to give two atomic species and an ultraviolet photon.

Both Deuterium and Hydrogen lamps emit radiation in the range 160 - 375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm.

Various UV radiation sources are as follows

a. Deuterium lamp
b. Hydrogen lamp
c. Tungsten lamp
d. Xenon discharge lamp
e. Mercury arc lamp

Various Visible radiation sources are as follows

a. Tungsten lamp
b. Mercury vapour lamp

c. Carbonone lamp

2. filters or monochromators:

All monochromators contain the following component parts;
• An entrance slit
• A collimating lens
• A dispersing device (a prism or a grating)
• A focusing lens
• An exit slit

Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

3. sample containers or sample cells: A variety of sample cells available for UV region. The choice of sample cell is based on
a) the path length, shape, size
b) the transmission characteristics at the desired wavelength
c) the relative expense

The cell holding the sample should be transparent to the wavelength region to be recorded. Quartz or fused silica cuvettes are required for spectroscopy in the UV region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000 nm. The thickness of the cell is generally 1 cm. cells may be rectangular in shape or cylindrical with flat ends.

4. Detectors: In order to detect radiation, three types of photosensitive devices are
a. photovoltaic cells or barrier- layer cell
b. phototubes or photo emissive tubes
c. photomultiplier tubes

Photovoltaic cell is also known as barrier layer or photonic cell. It consists of a metallic base plate like iron or aluminium which acts as one electrode. On its surface, a thin layer of a semiconductor metal like selenium is deposited. Then the surface of selenium is covered by a very thin layer of silver or gold which acts as a second collector tube.

When the radiation is incident upon the surface of selenium, electrons are generated at the selenium- silver surface and the electrons are collected by the silver. This accumulation at the silver surface creates an electric voltage difference between the silver surface and the basis of the cell. Phototubes are also known as photo emissive cells.

A phototube consists of an evacuated glass bulb. There is light sensitive cathode inside it. The inner surface of cathode is coated with light sensitive layer such as potassium oxide and silver oxide.

When radiation is incident upon a cathode, photoelectrons are emitted. These are collected by an anode. Then these are returned via external circuit. And by this process current is amplified and recorded.

The photomultiplier tube is a commonly used detector in UV spectroscopy. It consists of a photo emissive cathode (a cathode which emits electrons when struck by photons of radiation), several dynodes (which emit several electrons for each electron striking them) and an anode.

A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. These electrons are accelerated towards the first dynode (which is 90V more positive

than the cathode). The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated towards the second dynode, to produce more electrons which are accelerated towards dynode three and so on. Eventually, the electrons are collected at the anode. By this time, each original photon has produced 106 - 107 electrons. The resulting current is amplified and measured.

Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers; they are limited to measuring low power radiation.

Instrumentation
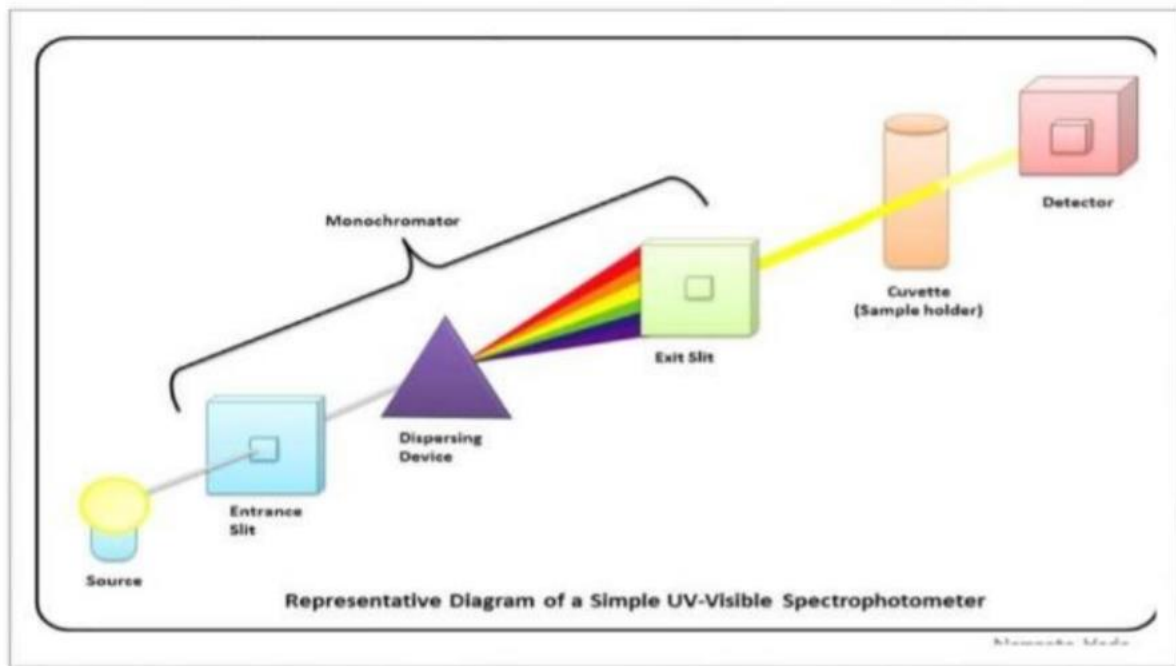
Representative Diagram of a Simple UV-Visible Spectrophotometer

Single Beam Spectrophotometer:

Single beam spectrophotometer is an analytical instrument in which all the light waves coming from the light source passes through the sample. Therefore, the measurements are taken as the intensity of light before and after the light pass through the sample. These single beam spectrophotometers are more compact and optically simpler than double beam spectrophotometers. And also, these instruments are less expensive.


Single Beam Spectrophotometer
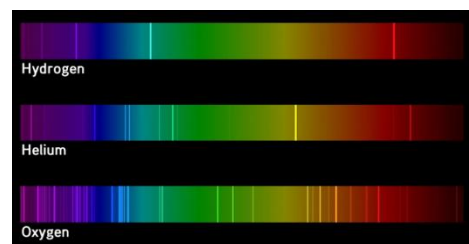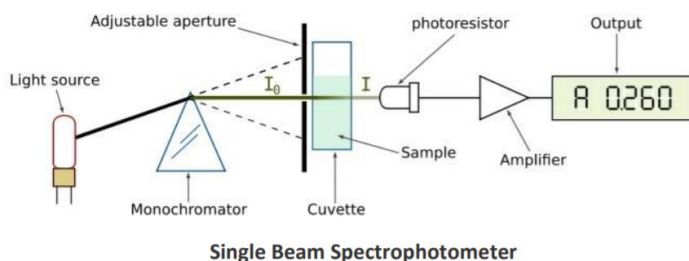
The sensitivity of detection of the light beam after it passes through the sample is high since it uses a non-split light beam (therefore, high energy exists throughout). Single beam spectrophotometers are available in analysis at visible and ultraviolet wavelength ranges.

A single beam spectrophotometer measures the concentration of an analyte in a sample by measuring the amount of light absorbed by that analyte. Here, the Beer Lambert Law comes into operation. This law states that the concentration of an analyte is directly proportional to the absorbance.

Double Beam Spectrophotometer:

Double beam spectrophotometer is an analytical instrument in which the light beam coming from the light source splits into two fractions. One fraction act as the reference (the reference beam) while the other fraction passes through the sample (sample beam). As a result, the reference beam does not pass through the sample.
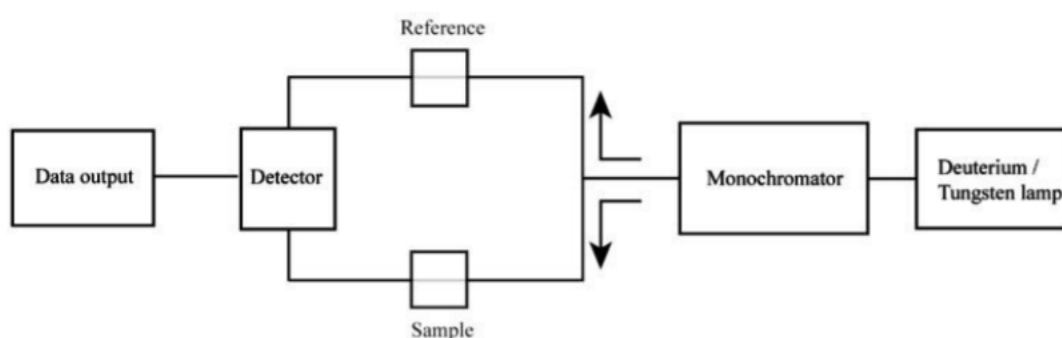
Metal Ligand Equilibria and Reaction Mechanism of Transition Metal Complexes

Determination of Constant by Job's method:

1. **Learning OUT COME:** After studying this module, you shall be able to know about

- Formation and Stability of Inorganic Complexes in Solution
- Optical Methods for obtaining the stoichiometry of complex (determination of the composition of complexes)
- Jobs method
- Limitations of jobs method

2. **Introduction:** The optical properties of complexes are governed by the formation of coordinate bonds between ligands and metal ions. The complexation in solution can easily be detected by various analytical instruments viz. uv-visible spectrophotometer, fluorimeter etc at very low concentrations. The basic conditions laid by Lambert-Beer law should be obeyed to selective determination of any species in solution.

3. **Binding Constants**: The binding constant (also known as association constant) is a type of the equilibrium constant (K). It is associated with the binding reaction of Metal (M) and ligand (A) molecules. $M + A \rightleftharpoons MA$

   At the equilibrium binding constant for forward reaction and dissociation constant for backward reaction is

   $K_f[M][A] = K_b[MA]$ The overall constant of the reaction is called binding constant

   $K_a = K_f/K_b = [MA]/[M][A]$

   The units of K_f and K_b are of $M^{-1} s^{-1}$ and s^{-1}, respectively, while the binding constant (K_a) is of unitless values

4. **Methods for obtaining the stoichiometry of complex:**

   Methods for obtaining the stoichiometry of complex (determination of the composition of complexes)

   $nA + mM \longrightarrow A_nM_m$ There are three common optical methods for the determination of the composition of complexes.

   Continuous-variation method (Job's method): This method is based on the measurement of absorption of a series of solutions in which molar concentrations of two reactants vary but their sum remains constant.

   Mole-ratio method: This method is based on the measurement of absorption of a series of solution in which the analytical concentration of one reactant is held constant while that of other is varied.

   Slope-ratio method: In this method, the reaction can be forced to completion with a large excess of either metal or ligand. It is used for studying weak complexes.

Continuous-variation method (Job's method): This method is also known as the method of continuous variation. The principle of the method is that the mole-ratio of the metal ion and the ligand is varied between 0 and 1 at constant total concentration $C = C_L+C_M$ and the absorbance of the solutions of different composition is measured. The absorbance is then plotted against the mole fraction of the ligand(x_L). If only one complex species has been formed, with composition ML_n and the absorbance is measured at a wavelength where neither the metal ion nor the ligand but only the complex absorbs, then n, the average number of ligands bound by one metal ion, can be calculated from the abscissa of the maximum of the curve (x_{max}):

$$n = \frac{x_{max}}{1 - x_{max}}$$

This is a very common method for determination of composition of complexes. Equimolar mixture of metal and ligand are taken and are mixed to give a series of solution having the same total concentration of metal and ligand, but varying the concentration of metal and ligand. Table below shows such a set of solutions

	$T_M \times 10^{-2}$ M	$T_A \times 10^{-2}$ M	$(T_A + T_A) \times 10^{-2}$ M
1)	10	0	10
2)	9	1	10
3)	8	2	10
4)	7	3	10
5)	6	4	10
6)	5	5	10
7)	4	6	10
8)	3	7	10
9)	2	8	10
10)	1	9	10
11)	0	10	10

Consider a complex reaction: M + nA $\Leftrightarrow$ MAn

(1 - x) x

$K = \dfrac{[MA_n]}{[M][A]^n}$ $or, [MA_n] = K[M][A]^n$ ... (1)

Suppose x is the mole fraction of ligand and (1 - x) is the mole fraction of metal present in the solution. The total number of moles of reactants present in solution at equilibrium if, N (no. of moles of meal + no. of moles of ligand) in one liter of solution, [M] the free metal, [L] free ligand and concentration of complex are given by the equations

$$[M] = T_M - [MA_n] = (1 - x)N - [MA_n] \ldots\ldots\ldots\ldots\ldots. (2)$$

$$[M] = T_A - n[MA_n] = xN - n[MA_n] \ldots\ldots\ldots\ldots\ldots. (2)$$

Where T_M and T_L are the total metal and ligand concentrations. Differentiating w.r.t. x and applying the condition of equilibrium for maximum complex formation:

(1) $\dfrac{d[MA_n]}{dx} = 0$

(2) $\dfrac{d[M]}{dx} = -N$

(3) $\dfrac{d[A]}{dx} = N$ $\{[A] = (x)N\}$

$$\Rightarrow \quad \frac{d}{dx}\left([M][A]^n\right)=0$$

$$\Rightarrow \quad [M]\frac{d}{dx}[A]^n + [A]^n\frac{d[M]}{dx}=0$$

$$\Rightarrow \quad [A]^n\frac{d[M]}{dx} + n[M][A]^{n-1}\frac{d}{dx}[A]=0$$

Substitute the value of $\dfrac{d[M]}{dx}$ and $\dfrac{d[A]}{dx}$ in (4)

$$[A]^n(-N) + n[M][A]^{n-1}N = 0$$

$$\Rightarrow \quad N\left[n[M][A]^{n-1} - [A]^n\right] = 0$$

$$\Rightarrow \quad (-N)[A]^n = -nN[M][A]^{n-1}$$

$$\Rightarrow \quad [A] = n[M]$$

Substitute the value of $[A]\,\&\,[M]$ from equation 2 and 3:

$$xN - n[MA_n] = n\big[(1-x)N - [MA_n]\big]$$

$$\Rightarrow \quad xN - n[MA_n] = n(1-x)x - n[MA_n]$$

$$\Rightarrow \quad xN - n[MA_n] = nN - nNx - n[MA_n]$$

$$\Rightarrow \quad xN + nNx = nN + n[MAn] - n[MA_n]$$

$$\Rightarrow \quad Nn(1-x) = xN$$

$$\Rightarrow \quad n = \frac{x}{1-x}$$

So, on drawing the graph between absorbance of prepared series of solution and their corresponding mole fraction, the exact ratio of metal and ligand at equilibrium can be observed at maxima of the graph. For all the cases of graph drawn below, consider absorbance on ordinate and mole fraction on abscissa
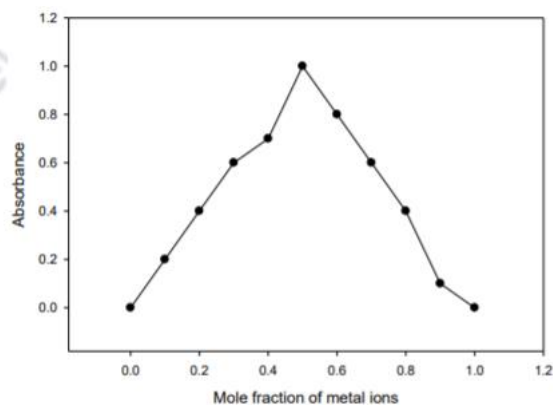

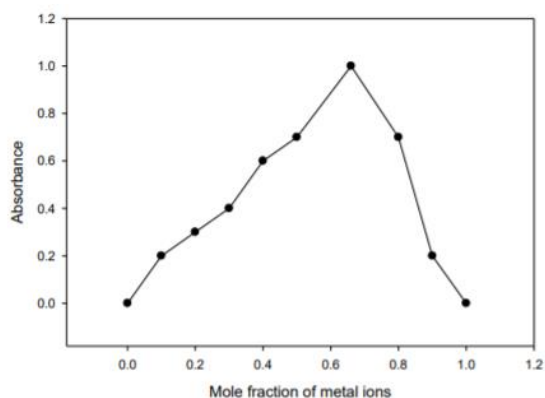Figure 1: For 1:1 case between metal and ligand

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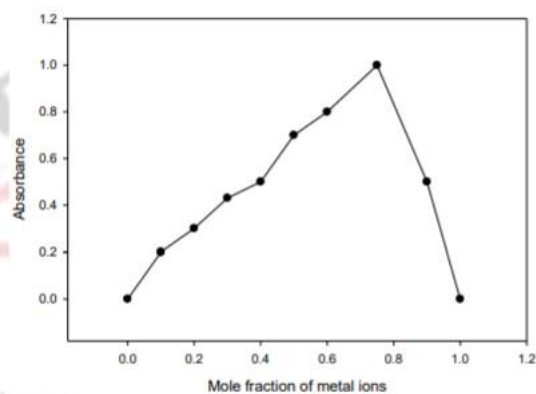Figure 2: For 1:2 case between metal and ligand

Figure 3: For 1:3 case between metal and ligand

Let at this pt x 0.5 ligand is 0.5 and metal is 0.5.

∴ total mole fraction is 1 *i.e.* it is 1:1 complex.

For 1:2, $x = 0.67$ & 1:3, $x = 0.75$.

For strong ionic compounds, pH should be maintained during the measurement of the spectra. Job's method is also used for calculating approx. value of β.

6. Limitations

1) This method is applicable to one type of equilibria i.e., only one type of complex formation in the solution.

2) This is applicable to moderate stable complexes; it means it cannot be applied to very weak complexes.

3) If the complexes are colourless, then spectrophotometric method cannot be used. Measure the absorbance of prepared series of solution, according to Lambert's - Beer's law.

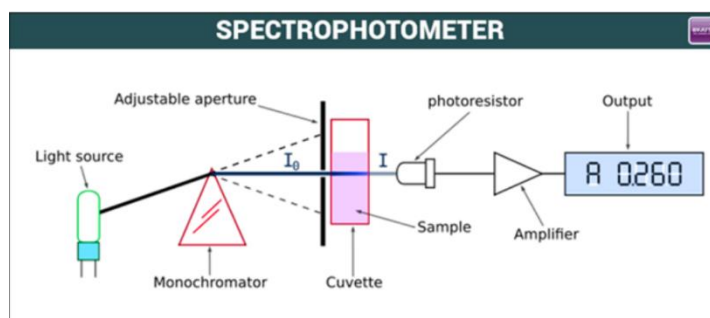4) pH and ionic strength must be maintained constant

7. Summary

  ➢ The binding constant (also known as association constant) is a type of the equilibrium constant (K).
  ➢ Continuous-variation method (Job's method), Mole-ratio method and Slope-ratio method are the common methods for obtaining the stoichiometry of complex (determination of the composition of complexes).
  ➢ Job's method is based on the measurement of absorption of a series of solutions in which molar concentrations of two reactants vary but their total sum remains constant

How you can use spectrophotometer to measure the concentration of a transition metal ion in solution:

Using the Beer-Lambert Law to measure the unknown concentration of a transition metal ion in solution.

Spectrophotometry is used to measure the concentration of a metal's ion in solution. In Spectrophotometry, we measure how much visible light a metals solution of a given concentration is absorbing. The measurements are taken using a Spectrophotometer. (*Shown in diagram*).

The light passes through a filter**.** The filter selects the wavelength of light closest to maximum absorption. The coloured metal ion solution (in a cuvette) absorbs some of this light. The light absorbed is called the absorbance. The greater the concentration of coloured ions, the greater the absorbance. In less expensive spectrophotometers like those you have in college, you first zero the instrument using a cuvette of 'colorless' water. This sets readings to zero absorbance. Next you put in a cuvette of the coloured solution and read off the 'absorbance'. 'Zeroing' eliminates error because even a 'colorless blank' of cuvette and water can absorb a tiny amount of light.

These are step to estimate metal ions concentration using Lambert Beers Law:

1. *First, create a calibration curve of absorbance vs standard concentrations of metal ions and use it to measure the concentration of an unknown solution of your transition metal ion.*
2. *The absorbance of an intensely coloured transition metal ion in aqueous solution can be measured directly e.g., the concentration of manganese in the deep purple manganate (VII) ion, MnO_4^-.*
3. *But the absorbances of much less intensely coloured solutions of transition metals are more difficult to measure e.g., light blue hexaaquacopper(II) ions.*
4. *So, the thing to do is to create an intensely coloured solution using ligand exchange (use appropriate ligand to make metal-ligand complex which is colour solution gives strong absorbance). The intensely coloured solution then gives accurate measures of absorbance that can then be turned into accurate measures of concentration.*
5. *For example, add ammonia solution to the blue hexaaquacopper(II) ion to form the deep blue ammine complex. Or add potassium thiocyanate to a brown solution of Iron(III) ions to form the deep blood–red thiocyanate ion (SCN^-) complex.*

Creating the calibration curve:

1. *To do this, prepare a range of known concentrations of transition metal ion solution. Next, measure the absorbance of each of these solutions, preferably more than six, to establish a reliable calibration curve.*

2. *Next plot your results (see below) This plot shows results for the absorbance of different concentrations of copper (II) ions. Providing you work at reasonably low concentrations (probably $<10^{-2}M$), you will find that the calibration curve is a straight line (as above). In other words, it obeys a law, the Beer—Lambert Law: as we said above, the greater the concentration, the greater the absorbance.*

3. *Absorbance is directly proportional to the concentration of the aqueous solution. All you have to do now is take your solution of transition metal ion whose concentration you don't know, measure its absorbance and read off the concentration from the calibration curve.*
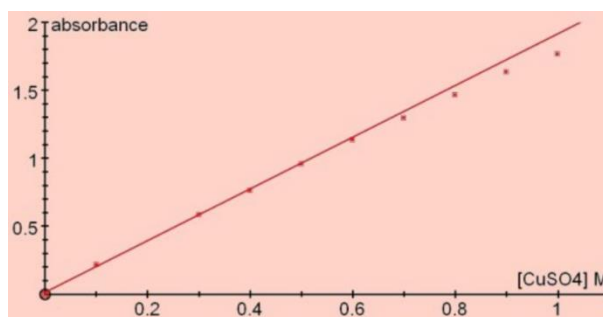
After measuring the absorbance of unknown metal ions and plot it in calibration curve. From the plot we can measured the concentration. Since, we know the total volume (V), concentration in mole/litre (c), and molecular weight (M_w) of metal salts. We can measure the amount of metal presents in solution using the formula $\frac{c.Mw.V}{1000}$ gram
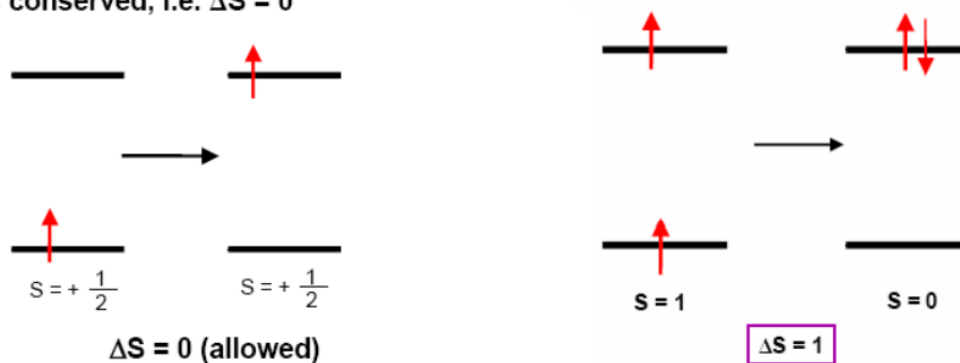
Selection Rules:

Selection rules for electronic transitions The Beer-Lambert Law $\mathbf{A = log_{10}(I_o/I) = \varepsilon c l}$ where ε is the molar extinction coefficient (in L cm^{-1} mole^{-1}), c is concentration in moleL^{-1} and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless. To explain the absorption spectra of coordination complexes, it is necessary to know the selection rules that govern electronic transitions. Any transition in violation of selection rule is said to be 'forbidden', but we will see how some rules are 'more forbidden than others. We shall not pursue the theoretical basis of the rules but merely outline simple tests for their application.

i. **Symmetry Selection Rule (The Laporte Rule):** In a molecule or ion possessing a centre of symmetry, transitions are not allowed between orbitals of the same parity, *for example d to d*. In other words, there must be change in parity ($\Delta l=\pm1$), i.e., the orbital quantum number should differ by 1. *The forbidden transitions are s → s, d → d, p → f. etc*. The geometries affected by this rule include octahedral and square-planar complexes. The rule is not applicable to tetrahedral complexes as it does not contain a center of symmetry.

ii. **Spin Selection rule:** *Any transition for which $\Delta S \neq 0$ is strongly forbidden*; that is, in order to be allowed, a transition must involve no change in spin state. Consider the case of the high spin d^5 complex $[Mn(H_2O)_6]^{2+}$. Electronic transition is not only Laporte forbidden but also spin forbidden. *Absorptions that are doubly forbidden transitions are extremely weak*. It is understandable, then, that dilute solutions of Mn(II) are colorless.

Promotion of an electron can only proceed if the spin orientation is conserved, i.e. $\Delta S = 0$

'forbidden' transitions

$S = +\frac{1}{2}$ $S = +\frac{1}{2}$

$\Delta S = 0$ (allowed)

$S = 1$ $S = 0$

$\Delta S = 1$

What is the CFSE of $[Fe(CN)_6]^{3-}$?

C.N. = 6 ∴ O_h Fe(III) ∴ d^5 h.s.   l.s. $CN^- = $ s.f.l.

+ 0.6 Δ_{oct}

- 0.4 Δ_{oct}

CFSE = 5 x - 0.4 Δ_{oct} + 2P = - 2.0 Δ_{oct} + 2P

Expected intensities of electronic transitions

Type of transition	Typical ε /dm³ mol⁻¹ cm⁻¹	Example
Spin-forbidden 'd-d'	< 1	$[Mn(OH_2)_6]^{2+}$ (high spin d^5)
Laporte-forbidden, spin-allowed 'd-d'	1-10	Centrosymmetric complexes, e.g. $[Ti(OH_2)_6]^{3+}$ (d^1)
	10-1000	Non-centrosymm. $[NiCl_4]^{2-}$
Charge transfer (fully allowed)	1000-50000	$[MnO_4]^{2-}$