Lecture 1

The Analytical Chemistry and Concept of the Instrumental Chemical Analysis

Analytical chemistry is the science concerned with diagnosing the identity and composition of substances and determining their ratio. That is, it can be divided into descriptive analytical chemistry and quantitative analytical chemistry.

Quantitative analytical chemistry is divided into traditional analytical chemistry (and this is not used in which devices are used and it is called solution chemistry). Whereas in the chemistry of instrumental analysis it depends on the use of devices mainly for quantitative or descriptive analysis and we are going to study it.

Any physical characteristic or property that the element or compound is characterized by can be the basis for one of the mechanical methods used in its analytics. Therefore, there are useful physical properties that can be adopted in automated analysis, including:

•Optical properties: they mean the interaction of radiation with matter, such as the phenomenon of radiation absorption and emission, radiation refraction, radiation scattering and radiation rotation

•Electrical properties: which depend on the electrochemical properties of the material involved in the analysis, including methods for measuring electrical voltage, electrical conductivity and the amount of electricity

•Various physical properties: which depend on different physical properties or characteristics of the materials in question, such as thermal properties, mass-to-charge ratio, and other properties.

It is clear from the above that the methods of automated analysis can be divided into:

1-Spectrophotometer Analysis Methods

2 -Electrical Analysis Methods

3 -Thermal Analysis Method

4 -Separation Chemical Methods

Through various modern automated analysis methods, it has become possible to obtain accurate and reliable results in all fields of science (medicine, pharmacy, agriculture, industry...etc). In addition to addressing many difficult and complex problems facing human beings. This is what made the automatic analysis distinguished from the traditional analysis with advantages, including- :

1-More sensitive (High Sensitivity) than traditional methods, as by automated methods we can reach small concentrations of up to one part per million (ppb.(

2- .More selective and more specific. Where the element or compound in question can be identified by the presence of other components.

3-Most of the automated methods are non-destructive so that the model is not destroyed. This is important in examining antiquities and artworks.

4- .Get the largest number of results in a short time and with less human effort.

*The choice of the type of method of automatic analysis in chemical analysis depends on a number of important factors that must be taken into account, including- :

1-The nature of the components of the sample or model under analysis. If it is solid, liquid, gas, organic or inorganic....etc

2- .The expected concentration of the substance if finding the concentration is required.

3-The limits and accuracy of the required results.

4- .Number of models and time available for analysis.

5 Amount and Availability of Sample Analysis

Lecture 2

Electromagnetic radiation and its effect on matter

Electromagnetic Radiation and its Interaction with Material

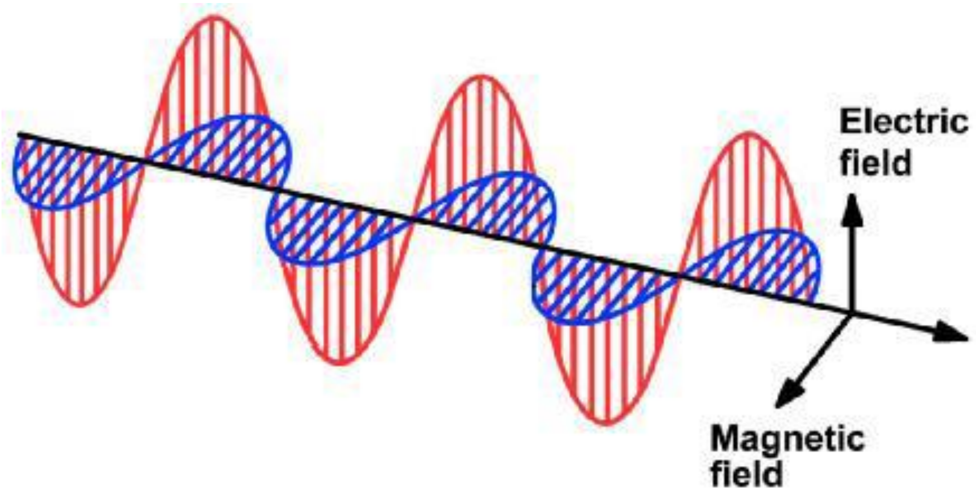
Electromagnetic radiation and theories related to the nature of radiation and what happens when radiation falls on the material must be known. Before discussing the types of spectral methods, how they work, and other matters related to them.

electromagnetic radiation

Electromagnetic radiation is a kind of soft energy that travels through a vacuum at a speed of (3 x 108 m/s). It takes various forms, such as light, radiant heat, X-rays, UV ultraviolet, visible light, IR-infrared, microwave radiation, and radio waves. A number of studies have shown that light has wave and particle properties.

•Wave Properties

The radiation propagates in the form of waves whose center is the source of the radiation and they travel in all directions at a speed of (3 x 108 m/s) through the vacuum.



Accordingly, the transmission of radiation in the form of waves includes both electric and magnetic forces, which led to the radiation being called electromagnetic radiation. An electric vehicle is the only one capable of interacting with matter and exchanging energy with it in normal conditions. Therefore, the electric field alone is concerned with the wave behavior.

The wave is characterized by characteristics and characteristics, such as wavelength, frequency, amplitude, and others.

Wave Length (ʎ)

It is the distance between two successive crests or troughs on the wave, or in a broader sense that the wavelength is the distance between two consecutive equal points on the wave. It is measured in units of length

Å = angstrom = 10^{-10} meter = 10^{-8} centimeter = 10^{-4} micrometer
nm = nanometer = 10^{-9} meter = 10 angstroms = 10^{-3} micrometer
μm = micrometer = 10^{-6} meter = 10^{4} angstroms

Frequency (ʋ)

It is the number of waves that pass a point in space in one second, and the unit is used (Hz/s)

*Frequency is a fixed value that does not change in the medium. The variable is the speed and length of the radiation wave from medium to medium.

Wave Number

It is the number of waves that pass in one centimeter and is measured in units (cm^{-1}). That is, it is the reciprocal of the wave number.

*The relationship between the speed of light, frequency and wavelength:

The relationship between the speed of light, frequency, and wavelength can be explained by the following equation:

$$\lambda = \frac{c}{\nu}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Amplitude

It is the distance between the wave's path line and the highest point at its crest or the lowest point at the base of the wave. The square of the amplitude indicates its intensity (I)

Through the wave characteristics of radiation, it was possible to explain many phenomena such as interference, diffraction, refraction and reflection that light shows.

Examples:

1-Calculate the frequency of the waves transmitted by a radio with a wavelength of 2.5 cm

*Did you know that the speed of electromagnetic waves per second is 3 x 10^{10} cm/s؟

2-If you know that the wavelength of yellow light is 0.6 x 10-6 m. Calculate both the frequency and the wave count for this radiation؟

•Properties Particle

Radiation consists of particles or packets called photons or quanta that have specific quantum energies and move through a vacuum at the speed of light.

And the scientist Planck expressed the energy of the photon by the following equation:

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

It is noted that the radiation energy is directly proportional to the frequency and inversely proportional to the wavelength. That is, a photon with a higher frequency (higher energy) has a wavelength

shorter while the lower frequency (lower energy) photon has a longer wavelength.

**Energy is often expressed in joules. The energy of a photon can be expressed in other units, such as the electron volt (1 ev = 1.6023×10^{-19}). To express the energy per mole, we need to multiply it by Avocado's number (6.023×10^{23}.)

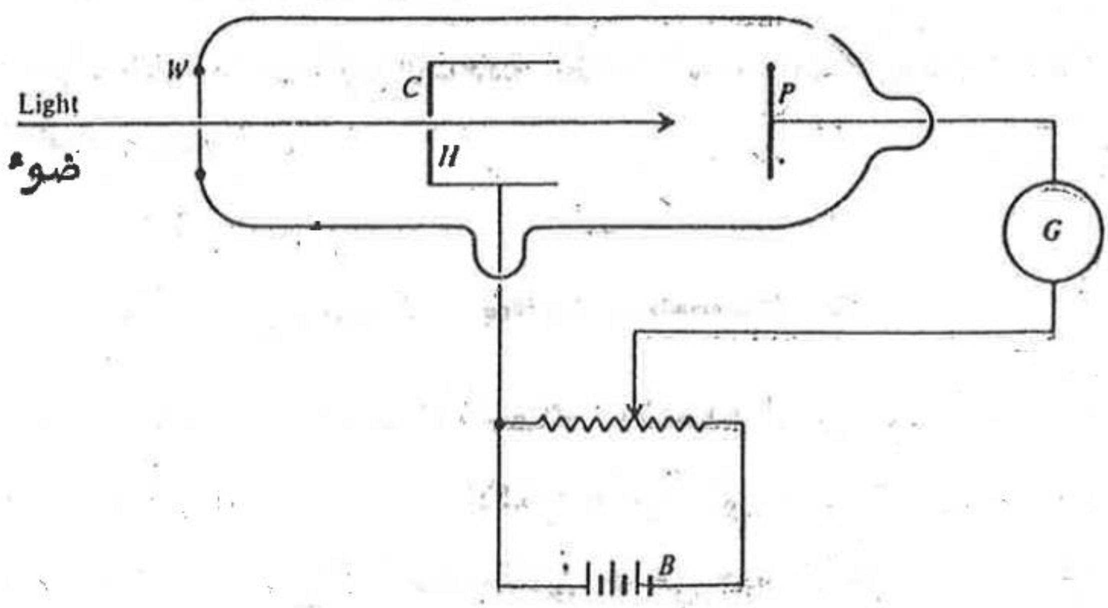
Example: Calculate the energy of radiation in units of electron volts if its wavelength is 1.2395×10^{-6} m?

Lecture 3

The Photoelectric Effect

This phenomenon is intended to be the release or emission of electrons from the surfaces of some sensitive metals when radiation has enough energy to liberate them. Like the release of electrons from the surfaces of some metals when radiation from the visible or violet region falls on them.

In the figure below is a schematic diagram of a device by which this phenomenon of the photoelectric effect can be studied using a vacuum tube of glass.



In general, the energy of a photon is calculated according to the following equation: $E=h\upsilon$

Therefore, the collision of sufficient radiation with the surface of a sensitive metal causes the emission of electrons with an energy related to the frequency of the incident radiation according to the relationship:

$E=h\upsilon - w_0$

E = energy of the emitted electron w_0 = work function

The work function is defined as the work (energy) needed to free the electron from the surface of the metal into the vacuum, and this is a distinct amount and is determined by the metal itself. As for heavy metals, such as cadmium, they have a high work function, which requires the fall of a high-energy beam such as ultraviolet rays to show the photoelectric effect.

$w_0 = h\,\upsilon_0$

Where the critical frequency (υ_0) is defined as the frequency required to remove an electron from the surface of the metal and release it without giving it any kinetic energy.

The following conclusions were obtained from this experiment:

1-Light can be considered one of the forms of energy capable of giving electrons sufficient energy

To overcome the bonding energy with the metal (work function, w0) and also gave it enough kinetic energy to overcome the repulsive forces with the anode.

2 -The intensity of the current passing from the cathode to the anode ((photocurrent) is proportional to the frequency and intensity of the ray falling on the cathode

3-The stopping voltage does not depend on the intensity of the incident light beam, and this can only be explained by assuming that the kinetic energy of the electrons emitted from the surface (E) does not exceed a maximum value that can be calculated from the following equation: $E=V_0e=1/2mV^2_{max}$

Electron charge = e, V_0 = stopping potential, m = mass of the electron, Vmax = maximum speed of the electron.

*The phenomenon of the photoelectric effect has been explained by the fact that the incident photon spends part of its energy (h υ) to free the electron from the surface of the metal, its amount is (w0), while the remaining part of the photon's energy is in the form of kinetic energy of the photoelectrons, and the final equation for calculating the kinetic energy of the liberated electron becomes as follows:

$E=h\,\upsilon - w_0$

$E = h(\upsilon - \upsilon 0)$

And Millikan was able, with precise experiments, to draw the relationship between kinetic energy and frequency for radiation

A monochromatic falls on the surface of a sensitive metal, where it obtains a straight line whose slope value represents

The Electromagnetic Spectrum

The electromagnetic spectrum can be divided into multiple regions according to the energy released. Where spectral studies showed that the electromagnetic spectrum contains all types of radiation as in the table below. It is noted that it is a continuous spectrum as a result of the gradation and overlap between its different wavelengths with each other, so that the boundaries separating the spectral regions of which it is composed are absent, and these limits are considered approximate. These areas are sandwiched between high-energy gamma rays and low-energy radio waves.

Type of Radiation	Wave Length m ،(ʎ)	Frequency Hz (υ)	Unit of measurement
Cosmic Rays	10^{-14}	10^{22}	A^0
Gamma Rays	10^{-11}	10^{19}	A^0
X-Rays	10^{-9}	10^{17}	A^0
Far Ultraviolet (U.V)	10^{-7}	10^{15}	nm
Near Ultraviolet (U.V)	10^{-7}	10^{15}	nm
Visible	10^{-6}	10^{14}	nm
Near Infrared	10^{-5}	10^{13}	cm^{-1}
Far Infrared	10^{-4}	10^{12}	µm
Microwave	10^{-3}	10^{11}	Hz
Radar	10^{-2}	10^{10}	Hz
Television	10^{0}	10^{8}	Hz
Nuclear Magnetic Resonance (NMR)	10	10^{7}	Hz
Radio	10^{2}	10^{6}	Hz
Alternating Current	10^{6}	10^{2}	Hz

The visible region that the human eye senses and is important to us occupies a very small portion of the total electromagnetic spectrum and its wavelengths lie between the limits (380-750 nm) and ultraviolet rays whose location is before the ultraviolet end of visible light (380 nm), while the infrared rays are The red that lies beyond the red end of visible light (750 nm).

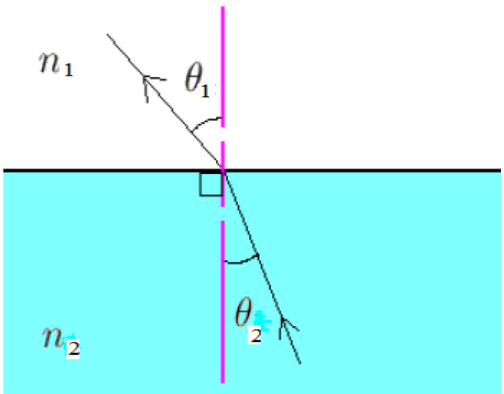
Lecture 4

Interaction of Electromagnetic Radiation with Matter

When the electromagnetic radiation interacts with matter, the electric field of the radiation will affect the atoms and particles of the medium. The nature and quality of the effect depends on the properties of the medium, and the reactance may lead to absorption, emission, scattering, reflection, or the radiation suffering from changes in its direction or polarization.

Refraction of Radiation

When a beam of light passes from one medium to another medium of different physical intensity, a change in the direction of the beam will be observed at the interface between the two media, and this phenomenon is called refraction.



This change in the direction of the beam is caused by the interference of the electric field of the radiation with the electrons of the medium, which results in a decrease in the speed or wavelength of the radiation without changing the radiation energy so that the frequency value remains constant.

The refractive index is a measure of the interaction between rays and the medium, and it is expressed by the following equation:

$\eta med = Vvac / Vmed$

Where: ηmed = refractive index of the medium at a known frequency

Vvac = velocity of radiation in a vacuum

Vmed = velocity of radiation in the medium

*The refractive index of air is (ηair), so the equation can be written as follows:

$\eta med = Vair / Vmed$

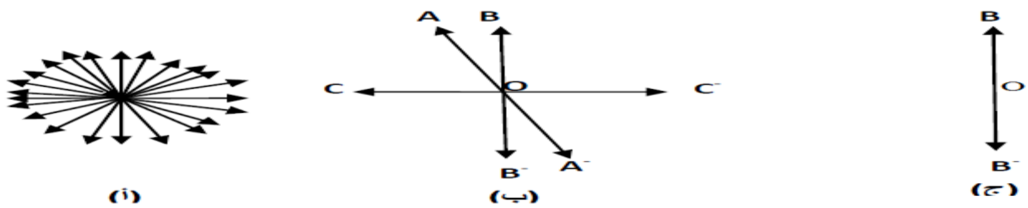
The process of refraction of light when passing from a less dense medium (air) to a denser medium (glass).

*Radiation velocity will be directly proportional to (SinΘ1) and (SinΘ2) in both mediums, so the refractive index

$\eta_{med} = (\sin\Theta_1) / (\sin\Theta_2)$

Polarization of Light and Optical activity

An ordinary light beam can be considered as a beam of waves whose electric waves oscillate in random directions and are all perpendicular to the beam's path as in the figure below (a). The electric vector in any one of the planes, such as the one oscillating in the direction (AOA), can be decomposed into two orthogonal components (BOB) and (COC) in the direction of the X and Y axes (b). The polarizer has the ability to remove one of the oscillation components, for example (COC) and allow the passage of (BOB) (c), and therefore the transmitted radiation has oscillation (vibration) in one level. The beam in this case is called a plane-polarized beam.



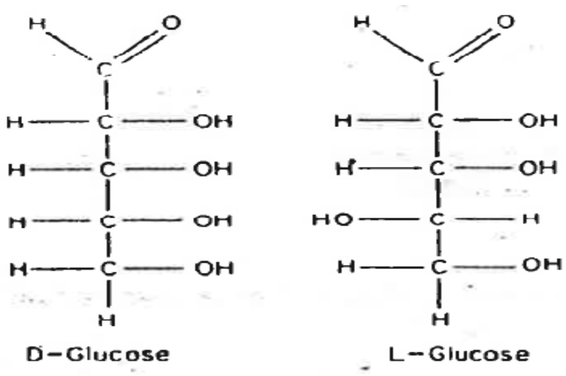
Polarization is of great importance in chemistry, as some crystals and liquids that do not have a center of symmetry can rotate the plane of polarized light that passes through them, as it suffers a rotation either to the right (clockwise) and is called right (+Dextrorotatory,) or to the left, and it is called (-Levorotatory). This phenomenon is known as the optical activity of the substance.

Substances and solutions are classified according to their behavior in the direction of polarized light into:

1-The first group: They are capable of changing the level (rotating) of polarization, and they are called optically active substances (Optically Active Substance). These materials include two main types:

a- Crystalline compounds, which lose their optical effectiveness when the crystal lattice is broken by dissolving, melting, or transitioning into a gas, such as quartz (SiO_2), sodium chlorate ($NaClO_3$) and some crystallized precipitates such as lead chloride ($PbCl_2$).

b-Compounds whose optical activity is attributed to asymmetry in their molecular structure, i.e. a lack of symmetry, and which maintain their optical activity regardless of the physical state, such as if they are liquid or gas (the reason for the asymmetry is the presence of a carbon atom connected to four different groups).). That is, they can be arranged by arranging one picture in the woman for the other, or as they are two pairs of hand gloves.



*The topic of polarimetry analysis, which is concerned with the study of optically active compounds. The amount of rotation for any compound depends- :

1-The type and concentration of particles contained in the medium

2- .The wavelength of polarized light

3-The distance the radiation travels through the sample (vessel length(

4- .The nature of the solvent.

5-Temperature.

*The sodium D line beam with wavelength λ=589.3 nm . is often used

**Specific rotation is considered a distinctive property of an optically active substance and is defined as the number of degrees observed caused by the passage of a distance polarized radiation through an optically active substance whose focus at a specific temperature and wavelength. Specific turnover can be calculated according to the following equation- :

$$[\alpha]_{\lambda}^{t_o} = \frac{100\alpha}{L * C}$$

α = empirically measured number of degrees of rotation

L = length of radiation path through the sample estimated (dm(

C = sample concentration in grams per 100 cm3

To calculate the specific rotation of the pure substance, replace the concentration with density (d) (g/cm^3).

$$[\alpha]_{\lambda}^{t_o} = \frac{\alpha}{L * d}$$

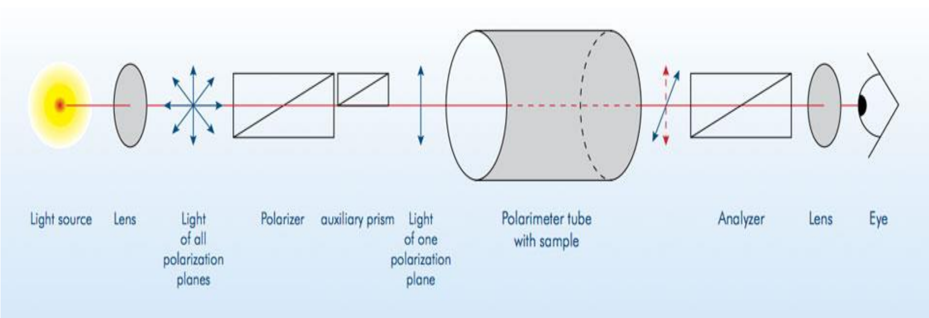
The specific rotation changes with the nature of the solvent, so it is indicated to mention the solvent used when measuring the specific gravity.

*There is another expression where it is used, which is the molecular rotation, which is calculated through the following equation- :

$$[M]_{\lambda}^{t_o} = \frac{[\alpha]_{\lambda}^{t_o} * M}{100}$$

M = molecular weight of the active substance

*Polarimetry: It is a device that measures the optical efficiency of optically active materials, and it consists of- :



1-Radiation source, a sodium vapor lamp with a filter is often used to remove all unwanted streaks.

2-Luminous lens to make the rays emitted from the lamp parallel

3 -Polarizer It produces plane polarized light like a Nicole prism.

4-A small Nicole prism, which is useful for enabling the examiner to reach the reading of the model by comparing the intensity of radiation before and after passing the model.

5 -A glass tube for placing the model under examination (0.5 dcm, 1 dcm, 2 dcm).

6-The analyzer is used to follow the polarized light coming out of the model.

7 -Optical lenses and a scale to measure the angle of rotation. It may be connected to the device with a digital recorder or calculator for the purpose of reading in digital form

*The most important applications of polarization- :

1 -Descriptive analysis: The specific rotation of a pure compound under certain conditions represents a useful physical constant for diagnostic purposes, such as the importance of other physical constants such as melting point, boiling point, refractive index...etc.

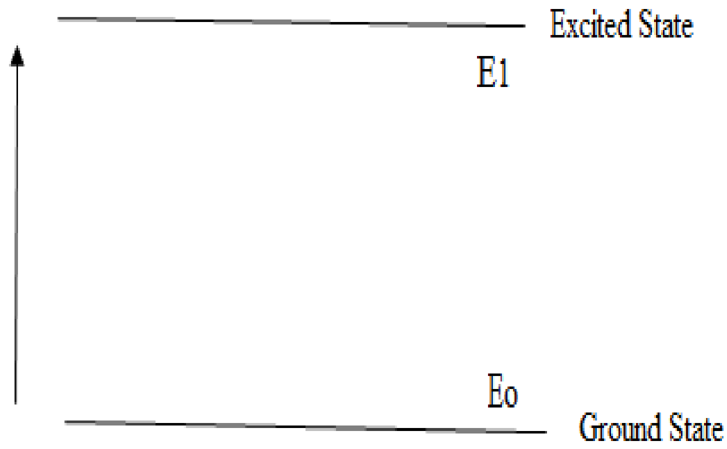
2 -Quantitative analysis: Polarization measurements are used to quantitatively analyze optically active materials by relating the rotation and concentration to a calibration curve.

3- Determine the weight of the molecule and study the kinetics of chemical reactions

Lecture 5

Absorption of Radiation

Absorption means the disappearance of part of the frequencies of the wave ray when it passes through a medium (gas - liquid - solid). In other words, the interference of the beam with matter results in a transfer of energy from the ray beam to matter and this results in the transfer of the absorbing particles of the beam's energy to higher energy levels From its level of rest or stability, ground state, it becomes in an excited state, and then returns to a stable state by the process of relaxation (relaxation).



$E=E_1 - E_o$

When a photon collides with matter, whether it is an atom, a molecule, an ion, there is a possibility for energy to be transferred to matter in a non-continuous process, meaning that the receiving substance either absorbs the entire photon's energy first. In the event that the substance absorbs the energy needed to excite it, and thus transfers it to a higher energy level

$$M + h\nu \rightarrow M^*$$

where M* represents the substance in the excited state. Just as the levels in atoms or molecules are locked, that is, for the excitation process to occur, the energy of the photon E must be equal to the energy required for the transfer of matter between the permissible energy levels, and on the contrary, absorption cannot occur. When the radiation absorption is measured against the wavelength of a specific solution, we obtain the Absorption Spectrum.

*Absorption spectra depend on some factors, including:

1-The physical state of matter.

2- .The quality of the absorbed rays

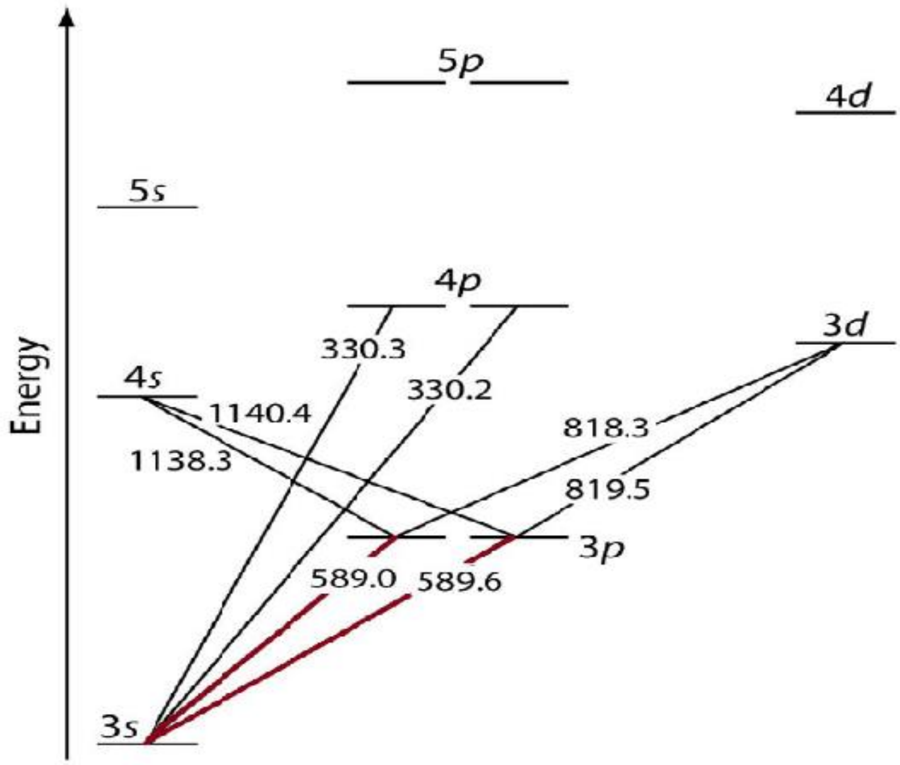
3-The nature of the radio-absorbing species

4- .The medium in which it is located

There are two types of absorption:

1-Atomic Absorption

This type of absorption occurs for monatomic particles as elemental sodium and mercury vapors. For example, the horizontal lines show the energy levels of the sodium atom and its (outer) valence electron, according to the electronic distribution of the sodium atom 1S2 2S2 2P6 3S1. Sodium is less than the bonding of the rest of the electrons because of its distance from the nucleus and the shielding factor that reduces the value of the charge affecting the nucleus on it.



The fall of radiation with a wavelength of (589 nm) pushes the electrons from the 3s energy level to a number of excited sodium atoms to move to the 3p energy level as a result of absorbing the energy needed for their excitation. on the floating difference between 3s and 3p. In the case of sodium, the energy emitted by the return of the excited electron is in the form of a beam of a specific wavelength, which is the common yellow color of a sodium flame.

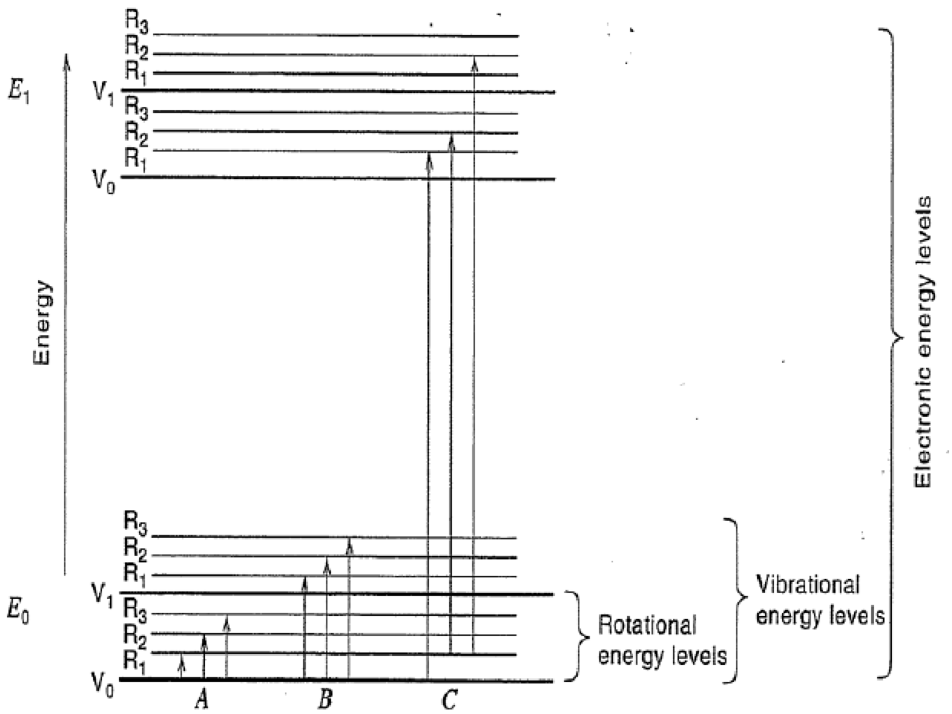
The simple case in which the electron rises to one energy level higher than its stability energy level and then returns to its original level is known as Resonance Absorption. As for the ray resulting from the return of the excited electron, it is called the Resonance Radiation. The phenomenon of resonance absorption is the basis of the technique used in the phenomenon of atomic absorption.

When the electron is given more energy, it will be more excited and excited and move to an energy level higher than the energy level 3P (to 4P or 5P). It matches the definition of resonant absorption. When using a high energy source, a number of electrons can be excited in addition to the outer valence electron in the element (the resulting beam can contain several wavelengths) and this represents the basis of the analysis method known as emission spectroscopy.

When the energy of the source is very high, it is possible that internal electrons are emitted from the atom. At that point, the electron descends from a higher energy level to fill the void caused by leaving the inner electron and the emitted photons are of high energy and on this basis X-rays are emitted from atoms when bombarded with fast-moving electrons.

2-Molecular Absorption

The process of radiation absorption by polyatomic molecules is more complex than in the case of atomic absorption because the number of potential energy levels is greater and more complex. The absorption of radiation by the molecules includes different types of energy transfers to different levels, as shown in the figure below.



Electronic Transition The energy required for electronic transmission is high energy and can only be provided by a high-energy beam (high frequency) represented in the visible and ultraviolet rays. Electronic transitions are accompanied by rotational and vibrational transitions, and this explains why the Uv spectrum appears in a wide range, in contrast to the IR spectrum.

•Vibration Transition The energy required for the vibrational transition is less than the energy of the electronic transition, as it includes the vibration of atoms or groups of atoms constituting the molecule in proportion to one another. Therefore, this transition occurs in the near and middle infrared region and is accompanied by rotational transitions.

Rotational transitions. In this transition, the molecule will absorb radiation and rise to a higher rotational level, and the molecule will rotate around different axes. This transition occurs in the far infrared region and the low-energy micro region (lower frequency.(

*The total energy of a molecule (ETotal) is

ETotal = Eele + Evib + Erot

Emission of Radiation

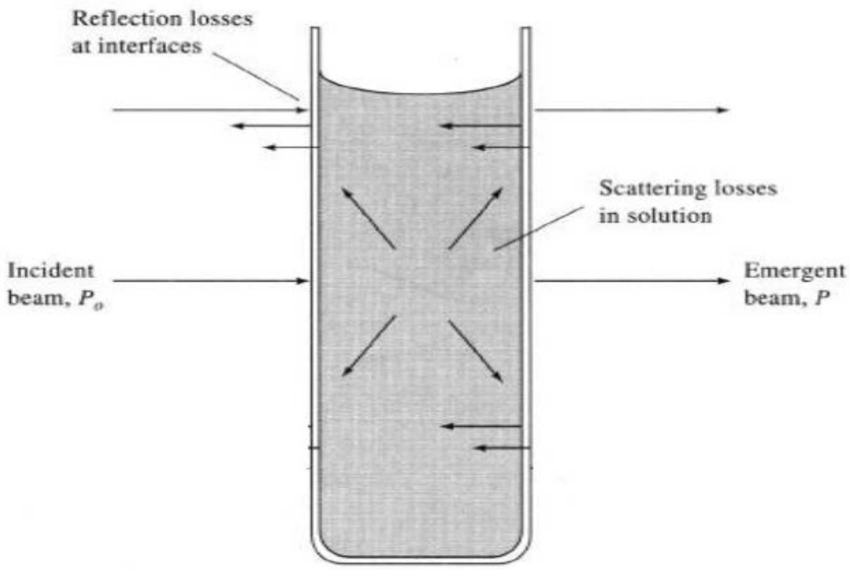
It is the process that includes the conversion of part of the internal energy acquired by the excited substance into emitted radioactive energy. It is the opposite of the absorption process.

After the molecule absorbs an appropriate energy, it moves from the steady state to any of the energy levels associated with the electronic level in the excited state and remains excited for a period ranging from (10^{-9})

Lecture 6

Quantitative analysis by absorbing electromagnetic radiation

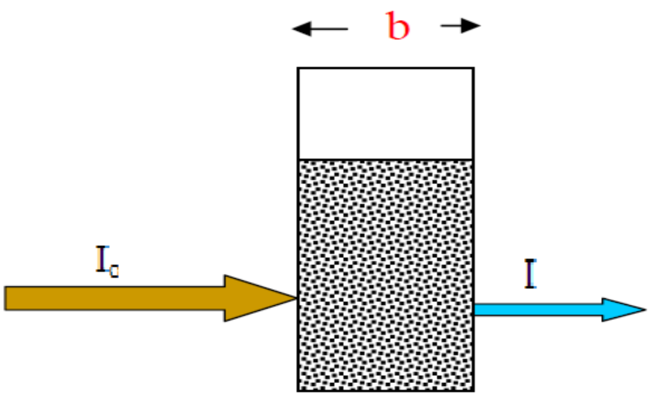
If a radiation beam is passed through a glass container containing a solution, the light beam emerging from the container will be less than the strength of the original incident beam, and this decrease may be due to reflection (air-glass) or scattering (particles suspended in the solution). The main reason for the decrease in the power of the penetrating rays may be the absorption of radiation energy by the solution particles.



In the event that the absorbed beam is visible light, the transmitted beam may appear as a complementary color to the color absorbed in the solution. Below is a table showing the absorbed color and its complementary color

Relationship between absorption, transmittance and concentration (Beer-Lambert law)

When parallel monochromatic rays of intensity Io are directed perpendicular to one side of the vessel and after passing a distance b through the sample containing N absorbing particles (atoms, ions or molecules), the intensity of the transmitting radiation I decreases from the other side as in the figure below- :



It is clear that the intensity of radiation decreases as it penetrates to a farther distance inside the vessel, as well as the higher the number of radioactive particles (concentration of the substance). The quantitative expression of this relationship is what is known as the Beer-Lambert Law, which contains (the successive increase in the number of identical radiation-absorbing particles falling in the path of a beam of monochromatic radiation absorb equal parts of the radiation energy that passes through it). And the mathematical relationship of this law is:

$$A = \varepsilon b c$$

Where (A) Absorbance and (ε) Molar absorptivity (C) Molar concentration (Mole/L), this is for a substance whose molecular weight is known. As for substances whose nature and molecular weight are not specified, their concentration is expressed (g/L).) and replace (ε) with the constant (a), which is known as Specific Absorptivity, so the relationship becomes as follows:

$$A=abc$$

*As for the percentage of the transmitted radiation, it is calculated through the equation:

$$T\% = \frac{I_t}{I_0} * 100$$

T = permeability, and permeability can be linked with absorbance through the following equation:

$$A = -\log T = log\frac{1}{T} = log\frac{I_0}{I_t} = \in bc$$

*Duty to prove the validity of the relationship: A=2.00 - log T%

*The most important things that must be taken into account in order for the Beer-Lambert law to be true are:

1 -The incident radiation is monochromatic radiation.

2 -The radiation-absorbing particles act independently among themselves in the absorption attic.

3-Absorption is induced in a regular dimensional cross section

4 -The energy decomposition is very fast so that fluorescence does not occur

5-The refractive index of the solution does not depend on the concentration (which is not true at high concentrations).

* The figure below shows the relationship between absorption or percentage and concentration: