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UNIT 1 ELEMENTARY QUANTUM MECHANICS

Structure

1.1 INTRODUCTION

The field of quantum mechanics concerns the description of phenomenon on small scales to which classical physics breaks it down. The biggest difference between the classical and microscopic realm is that the quantum world cannot be perceived directly but rather through the use of instruments and a key assumption to quantum physics is that quantum mechanical principles must reduce to Newtonian principles at the macroscopic level (there is a continuity between quantum and Newtonian mechanics).

Quantum mechanics was capable of bringing order to the uncertainty of the microscopic world by treatment of the wave function with new mathematics. Key to this idea was the fact that relative probabilities of different possible states are still determined by laws. Thus, there is a difference between the role of chance in quantum mechanics and the unrestricted chaos of a lawless Universe.

Every quantum particle is characterized by a wave function. In 1925 Erwin Schrodinger developed the differential equation which describes the evolution of those wave functions. By using Schrodinger equation, scientists can find the wave function which solves a particular problem in quantum mechanics. Unfortunately, it is usually impossible to find an exact solution to the equation, so certain assumptions are used in order to obtain an approximate answer for each particular problem.

Although it is the modern theory of quantum mechanics in which we are primarily interested because of its applications to chemical problems, it is desirable for us first to discuss briefly the background of classical mechanics from which it was developed.

1.1.1 THE OLD QUANTUM THEORY

The old quantum theory was born in 1900, when Max Planck announced his theoretical derivation of the distribution law for, black-body radiation which he had previously formulated from empirical considerations. He showed that the results of experiment on the distribution of energy with frequency of radiation in equilibrium with matter at a given temperature can be accounted for, by postulating that the vibrating particles of matter (considered to act as harmonic oscillators) do not emit or absorb light continuously, but instead, only in discrete quantities of magnitude (hν) proportional to the frequency (ν) of the light. The constant of proportionality, is a new constant of nature; it is called Planck's constant (h) and has the magnitude $6.547 \times 10^{\sim 27}$ erg sec. Its dimensions (energy × time) are those of the old dynamical quantity called action; they are such that the product of h and frequency ν (with dimensions sec^{-1}) has the dimensions of energy. The dimensions of h are also those of angular momentum and we shall see later that just as hν is a quantum of radiant energy of frequency ν, so is h/2ω a natural unit or quantum of angular momentum.

The development of the quantum theory was at first slow. It was not until 1905 that Einstein suggested that the quantity of radiant energy hν was sent out in the process of emission of light not in all directions but instead unidirectionally, like a particle. The name ‘light quantum’ or ‘photon’ is applied to such a portion of radiant energy. Einstein also discussed the photoelectric effect, the fundamental processes of photochemistry and the heat capacities of solid bodies in terms of the quantum theory. When light falls on a metal plate, electrons are emitted from it. The maximum speed of these photoelectrons, however is not dependent on the intensity of the light, as would be expected from classical electromagnetic theory but only on its frequency; Einstein pointed out that this is to be expected from the quantum theory, the process of photoelectric emission involving the conversion of the energy (hν) of one photon into the kinetic energy of a photoelectron (plus the energy required to remove the electron from the metal). Similarly, Einstein's law of photochemical equivalence states that one molecule may be activated to chemical reaction by the absorption of one photon.

The third application, to the heat capacities of solid bodies, marked the beginning of the quantum theory of material systems. Planck's postulate regarding the emission and absorption of radiation in quanta hν suggested that a dynamical system such as an atom oscillating about an equilibrium position with frequency νQ might not be able to oscillate with arbitrary energy but only with energy values which differ from one another by integral multiples of hνQ. From this assumption and a simple extension of the principles of statistical mechanics it can be shown that the heat capacity of a solid aggregate of particles should not remain constant with decreasing temperature but should at some low temperature fall off rapidly toward zero.

This prediction of Einstein, supported by the earlier experimental work of Dewar on diamond was immediately verified by the experiments of Nernst and Eucken on various substances and quantitative agreement between theory and experiment for simple crystals was achieved through Debye's brilliant refinement of the theory.

Classical physics tends to deal with numbers such as the position, velocity and acceleration of particles. However, quantum mechanics deals primarily with functions rather than with numbers. To facilitate manipulating functions, they will be modeled as vectors in infinitely many dimensions. Dot products, lengths and orthogonality can then all be used to manipulate functions. Dot products will however be renamed to be “inner products” and lengths to be “norms.” “Operators” will be defined that turn functions into other functions. Particularly important for quantum mechanics are “eigen value” cases, in which an operator turns a function into a simple multiple of itself.

A special class of operators, “Hamiltonion” operators will be defined. These will eventually turn out to be very important, because quantum mechanics associates physical quantities like position, momentum and energy with corresponding Halmiltonion operators and their eigen values.

Objectives

After studying this unit, you should be able to know

- about black body radiation,
- to understand different black body radiation laws
- define photoelectric effect, Compton effect, Heisenberg uncertainity principle, degree of freedom
- explain heat capacity of solids, Bohr’s model of hydrogen atom, De broglie’s hypothesis, Hamiltonion operator
- to understand statement of Born Oppenheimer approximation

1.2 BLACK-BODY RADIATION

A “blackbody” refers to an opaque object that emits “thermal radiation”. A perfect blackbody is one that absorbs all incoming light and does not reflect any. At room temperature, such an object would appear to be perfectly black (hence the term blackbody). However, if heated to a high temperature, a blackbody will begin to glow with thermal radiation.

In fact, all objects emit thermal radiation (as long as their temperature is above Absolute Zero, or -273.15 degrees Celsius), but no object emits thermal radiation perfectly; rather, they are better at emitting/absorbing some wavelengths of light than others. These uneven efficiencies make it difficult to study the interaction of light, heat and matter using normal objects.

Fortunately, it is possible to construct a nearly-perfect blackbody. Construct a box made of a thermally conductive material, such as metal. The box should be completely closed on all sides, so that the inside forms a cavity that does not receive light from the surroundings. Then, make a small hole somewhere on the box. The light coming out of this hole will almost perfectly resemble the light from an ideal blackbody, for the temperature of the air inside the box.

At the beginning of the 20th century, scientists Lord Rayleigh and Max Planck (among others) studied the blackbody radiation using such a device. After much work, Planck was able to empirically describe the intensity of light emitted by a blackbody as a function of wavelength. Furthermore, he was able to describe how this spectrum would change as the temperature changed. Planck's work on blackbody radiation is one of the areas of Physics that led to the foundation of the wonderful science of Quantum Mechanics but that is unfortunately beyond the scope of this article.

What Planck and the others found was that as the temperature of a blackbody increases, the total amount of light emitted per second increases, and the wavelength of the spectrum's peak shifts to bluer colours (see Figure 1).

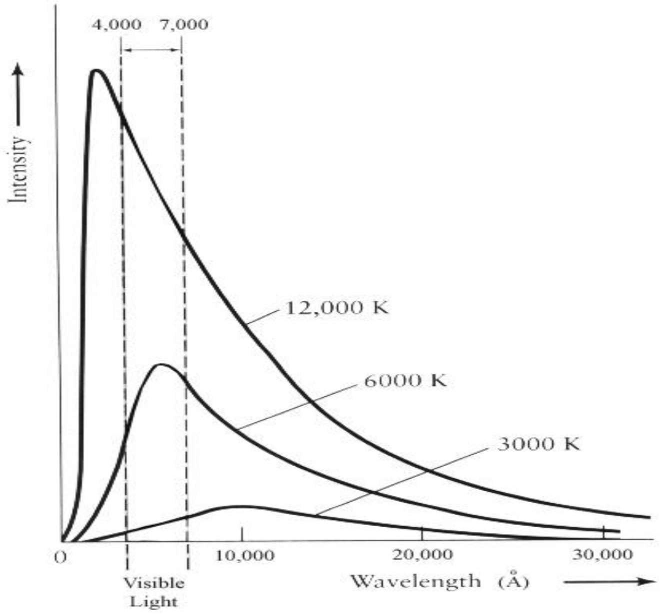


Figure 1

For example, an iron bar becomes orange-red when heated to high temperatures and its colour progressively shifts toward blue and white as it is heated further.

In 1893, German physicist Wilhelm Wien quantified the relationship between blackbody temperature and the wavelength of the spectral peak with the following equation:

$$\lambda_{max} \cdot T = 0.29\ cm\ K$$

where T is the temperature in Kelvin. Wien's law (also known as Wien's displacement law) states that the wavelength of maximum emission from a blackbody is inversely proportional to its temperature. This makes sense; shorter-wavelength (higher-frequency) light corresponds to higher-energy photons, which you would expect from a higher-temperature object.

For example, the sun has an average temperature of 5800 K, so its wavelength of maximum emission is given by:

$$\lambda_{max} = \frac{0.29\ cm}{5800} = 500\ nm$$

This wavelengths falls in the green region of the visible light spectrum, but the sun's continuum radiates photons both longer and shorter than lambda(max) and the human eyes perceives the sun's colour as yellow/white.

In 1879, Austrian physicist Stephan Josef Stefan showed that the luminosity, L, of a black body is proportional to the 4th power of its temperature T.

$$L = A \cdot \alpha \cdot T^4$$

where A is the surface area, alpha is a constant of proportionality and T is the temperature in Kelvin. That is, if we double the temperature (e.g. 1000 K to 2000 K) then the total energy radiated from a blackbody increase by a factor of 2^4 or 16.

Five years later, Austrian physicist Ludwig Boltzman derived the same equation and is now known as the Stefan-Boltzman law. If we assume a spherical star with radius R, then the luminosity of such a star is

$$L = 4\pi R^2 \cdot \alpha \cdot T^4$$

where R is the star radius in cm and the alpha is the Stefan-Boltzman constant, which has the value:

$$\alpha = 5.670 \cdot 10^{-5}\ ergs/s/cm^2/K^{-4}$$

1.3 PLANCK'S RADIATION LAW

The primary law governing blackbody radiation is the Planck Radiation Law, which governs the intensity of radiation emitted by unit surface area into a fixed direction (solid angle) from the blackbody as a function of wavelength for a fixed temperature. The Planck Law can be expressed through the following equation.

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

$h = 6.625 \times 10^{-27}$ erg- sec (Planck Constant)

$k = 1.38 \times 10^{-16}$ erg/ K (Boltzmann Constant)

$c = 3 \times 10^{10}$ cm/sec (Speed of Light)

The behaviour is illustrated in the figure 2 shown above. The Planck Law gives a distribution that peaks at a certain wavelength, the peak shifts to shorter wavelengths for higher temperatures and the area under the curve grows rapidly with increasing temperature.

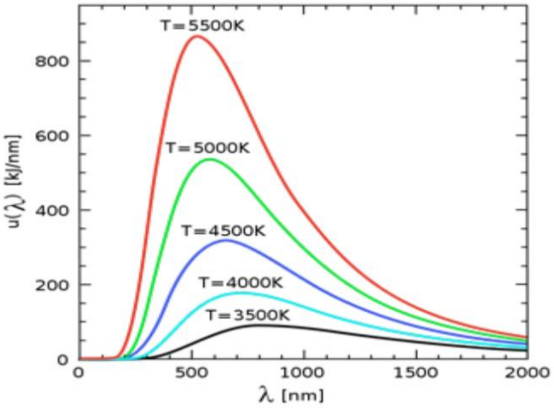


Figure 2

1.4 PHOTOELECTRIC EFFECT

Photoelectric effect is a phenomenon in which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. The effect is often defined as the ejection of electrons from a metal plate when light falls on it. In a broader definition, the radiant energy may be infrared, visible or ultraviolet light, X-rays or gamma rays; the material may be a solid, liquid or gas and the released particles may be ions (electrically charged atoms or molecules) as well as electrons. The phenomenon was fundamentally significant in the development of modern physics because of the puzzling questions it raised about the nature of light-particle versus wavelike behaviour that were finally resolved by Albert Einstein in 1905. The effect remains important for research in areas from materials science to astrophysics, as well as forming the basis for a variety of useful devices.

1.4.1 Photoelectric principles

According to quantum mechanics, electrons bound to atoms in specific electronic configurations. The highest energy configuration (or energy band) that is normally occupied by electrons for a given material is known as the valence band, and the degree to which it is filled largely determines the material's electrical conductivity. In a typical conductor (metal), the valence band is about half filled with electrons, which readily move from atom to atom, carrying a current. In a good insulator, such as glass or rubber, the valence band is filled and these valence electrons have very little mobility. Like insulators, semiconductors generally have their valence bands filled but unlike insulators, very little energy is required to excite an electron from the valence band to the next allowed energy band known as the conduction band because any electron excited to this higher energy level is relatively free. For example, the "bandgap" for Silicon is 1.12 eV (electron volts) and that of Gallium Arsenide is 1.42 eV. This is in the range of energy carried by photons of infrared and visible light, which can therefore raise electrons in semiconductors to the conduction band. (For comparison, an ordinary flashlight battery imparts 1.5 eV to each electron that passes through it. Much more energetic radiation is required to overcome the bandgap in insulators.) Depending on how the semiconducting material is configured, this radiation may enhance its electrical conductivity by adding to an electric current already induced by an applied voltage, or it may generate a voltage independently of any external voltage sources.

Photoconductivity arises from the electrons freed by the light and from a flow of positive charge as well. Electrons raised to the conduction band correspond to missing negative charges in the valence band, called "holes." Both electrons and holes increase current flow when the semiconductor is illuminated.

In the photovoltaic effect, a voltage is generated when the electrons freed by the incident light are separated from the holes that are generated, producing a difference in electrical potential. This is typically done by using a *p-n* junction rather than a pure semiconductor. A *p-n* junction occurs at the juncture between *p*-type (positive) and *n*-type (negative) semiconductors. These opposite regions are created by the addition of different impurities to produce excess electrons (*n*-type) or excess holes (*p*-type). Illumination frees electrons and holes on opposite sides of the junction to produce a voltage across the junction that can propel current, thereby converting light into electrical power.

Other photoelectric effects are caused by radiation at higher frequencies, such as X-rays and gamma rays. These higher-energy photons can even release electrons near the atomic nucleus, where they are tightly bound. When such an inner electron is ejected, a higher-energy outer electron quickly drops down to fill the vacancy. The excess energy results in the emission of one or more additional electrons from the atom, which is called the Auger effect.

Also seen at high photon energies is the Compton effect, which arises when an X-ray or gamma-ray photon collides with an electron. The effect can be analysed by the same principles that govern the collision between any two bodies, including conservation of momentum. The photon loses energy to the electron, a decrease that corresponds to an increased photon wavelength according to Einstein's relation [$E = hc/\lambda$]. When the collision is such that the electron and the photon part at right angles to each other, the photon's wavelength increases by a characteristic amount called the Compton wavelength, 2.43×10^{-12} metre.

1.4.2 Applications

Devices based on the photoelectric effect have several desirable properties, including producing a current that is directly proportional to light intensity and a very fast response time. One basic device is the photoelectric cell or photodiode. Originally, this was a phototube, a vacuum tube containing a cathode made of a metal with a small work function so that electrons would be easily emitted. The current released by the plate would be gathered by an anode held at a large positive voltage relative to the cathode. Phototubes have been replaced by semiconductor-based photodiodes that can detect light, measure its intensity, control other devices as a function of illumination, and turn light into electrical energy. These devices work at low voltages, comparable to their bandgaps and they are used in industrial process control, pollution monitoring, light detection within fibre optics telecommunication networks, solar cells, imaging and many other applications.

1.5 HEAT CAPACITY OF SOLIDS

Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49×10^{4} J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate). Each atom has an energy of $12k_BT$ where k_B is the Boltzmann constant and T is the absolute temperature. Thus,

$$c_V=6R2=3R$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids.

The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

1.5.1 Einstein’s theory of heat capacities

Einstein treated the atoms in a crystal as N simple harmonic oscillators, all having the same frequency νE. The frequency νE depends on the strength of the restoring force acting on the atom, i.e. the strength of the chemical bonds within the solid. Since the equation of motion for each atom decomposes into three independent equations for the x, y and z components of displacement, and N atom solid is equivalent to 3N harmonic oscillators, each vibrating independently at frequency νE.

Note that this treatment is a gross approximation, since in reality the lattice vibrations are very complicated coupled oscillations.

The energy levels of the harmonic oscillators are given by

$$\varepsilon_v = h\nu_E(v + ½),\ v = 0,\ 1,\ 2\ldots$$

Assuming the oscillators are in thermal equilibrium at temperature T, the partition function for a single oscillator is

$$q = \sum_{v=0}^{\infty} \exp[-\beta\varepsilon_v] = \sum_{v=0}^{\infty} \exp[-\beta h\nu_E(v+\tfrac{1}{2})] = e^{-x/2}\sum_{v=0}^{\infty} e^{-xv} = \frac{e^{-x/2}}{1-e^{-x}} \quad \text{where} \quad x = \beta h\nu_E.$$

where $x = \beta h\nu_E$.

In the above, we have used the fact that $\sum_{n=0}^{\infty} x^n = \frac{1}{1 - x}$.

The mean energy per oscillator is then

$$u = -\frac{d\ln q}{d\beta} = \frac{d}{d\beta}\left(\frac{\beta h\nu_E}{2} + \ln(1-e^{-\beta h\nu_E})\right) = \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E}-1}$$

The first term above, hν/2, is simply the zero point energy. Using the fact that energy is an extensive property, the energy of the 3N oscillators in the N-atom solid is

$$U = 3Nu = 3N\left(\frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E}-1}\right)$$

The heat capacity at constant volume is therefore

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3N\left(\frac{\partial U}{\partial \beta}\right)_v \frac{\partial \beta}{\partial T} = 3Nk\,\frac{x^2 e^x}{(e^x-1)^2} \quad \text{where} \quad x = \frac{h\nu_E}{kT} = \frac{\theta_E}{T}$$

θ_E is the ‘Einstein temperature’, which is different for each solid and reflects the rigidity of the lattice.

At the high temperature limit, when $T >> \theta_E$ (and $x << 1$), the Einstein heat capacity reduces to $C_v = 3Nk$, the Dulong and Petit law [prove by setting $e^x \sim 1+x$ in the denominator].

At the low temperature limit, when $T << \theta_E$ (and $x >> 1$), $C_V \rightarrow 0$ as $T \rightarrow 0$, as required by the third law of thermodynamics. [Prove by setting $e^x - 1 \sim e^x$ in the denominator for large x].

1.5.2 Debye’s theory of heat capacities

Debye improved on Einstein’s theory by treating the coupled vibrations of the solid in terms of 3N normal modes of vibration of the whole system, each with its own frequency. The lattice vibrations are therefore equivalent to 3N independent harmonic oscillators with these normal mode frequencies.

For low frequency vibrations, defined as those for which the wavelength is much greater than the atomic spacing, $\lambda >> a$, the crystal may be treated as a homogeneous elastic medium. The normal modes are the frequencies of the standing waves that are possible in the medium.

Debye derived an expression for the number of modes with frequency between ν and $(\nu + d\nu)$ in such a medium.

$$g(\nu)\,d\nu = \frac{4\pi V \nu^2}{v^3}\,d\nu = \alpha\,\nu^2 d\nu$$

where V is the crystal volume and v is the propagation velocity of the wave. As outlined above, this expression applies only to low frequency vibrations in a crystal. Debye used the approximation that it applied to all frequencies, and introduced a maximum frequency ν_D (the Debye frequency) such that there were 3N modes in total. i.e. $\int_0^{\nu_D} g(\nu)d\nu = 3N$. The Debye frequency corresponds to $\lambda = 2a$, when neighbouring atoms vibrate in antiphase with each other. With this approximation in place, Debye integrated over all of the frequencies to find the internal energy of the crystal, and then calculated the heat capacity using $C_v = \left(\frac{\partial U}{\partial T}\right)_v$ .The resulting expression is given below.

$$C_v = 3Nk\left(\frac{3}{x_D^3}\int_0^{x_D}\frac{x^4 e^x\,dx}{(e^x-1)^2}\right)$$

where $x = \frac{h\nu}{kT}$, and $x_D = \frac{h\nu_D}{kT} = \frac{\theta_D}{T}$. .The Debye heat capacity depends only on the Debye temperature θ_D.

The integral cannot be evaluated analytically, but the bracketed function is tabulated.

At high temperatures ($T \gg \theta_D$, $x_D \ll 1$), we may rewrite the integrand as follows:

$$\frac{x^4 e^x}{(e^x-1)^2} = \frac{x^4}{(e^x-1)(1-e^{x})} = \frac{x^4}{2(\cosh(x)-1)} = \frac{x^4}{2(x^2/2! + x^4/4! + \ldots)}$$

Retaining only the x^2 term in the denominator gives

$$C_v = 3Nk\left(\frac{3}{x_D^3}\int_0^{x_D} x^2\,dx\right) = 3Nk$$

To determine the low temperature limit ($T \ll \theta_D$, $x_D \gg 1$), we note that the integrand tends towards zero rapidly for large x. This allows us to replace the upper limit by ∞ and turn the integral into a standard integral, to give

$$C_v = 3Nk\left(\frac{T}{\theta_D}\right)^3\left(3\int_0^{\infty}\frac{x^4 e^x}{(e^x-1)^2}\right) = \frac{12}{5}\pi^4 Nk\left(\frac{T}{\theta_D}\right)^3$$

We see that the Debye heat capacity decreases as T^3 at low temperatures, in agreement with experimental observation. This is a marked improvement on Einstein’s theory.

1.6 BOHR’S MODEL OF HYDROGEN ATOM (NO DERIVATION) AND IT’S DEFECTS

Thomson’s atomic model and Rutherford’s atomic model failed to answer many questions related to the energy of an atom and its stability. In the year 1913, Niels Bohr proposed his atomic model, describing an atom as a small, positively charged nucleus surrounded by electrons that travel in circular orbits around the positively charged nucleus as planets around the sun in our solar system, with attraction provided by electrostatic forces. It was basically an improved version of Rutherford's atomic model overcoming its limitations. On most of the points, he is in agreement with him, like concepts of nucleus and electrons orbiting it. Salient features of Bohr's atomic model are:

1. Electrons revolve around the nucleus in stable orbits without emission of radiant energy. Each orbit has a definite energy and is called energy shell or energy level.
2. An orbit or energy level is designated as K, L, M, N shells. When the electron is in the lowest energy level, it is said to be in the ground state.
3. An electron emits or absorbs energy when it jumps from one orbit or energy level to another. When it jumps from higher energy level to lower energy level it emits energy while it absorbs energy when it jumps from lower energy level to higher energy level.
4. The energy absorbed or emitted is equal to the difference between the energies of the two energy levels (E_1, E_2) and is determined by Plank's equation.

$$\Delta E = E_2 - E_1 = h\nu$$

Where,

ΔE = energy absorbed or emitted
h = Plank's constant
ν = frequency of electromagnetic radiation emitted or absorbed

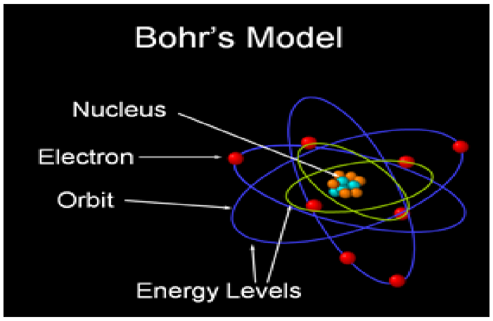
5. Angular momentum of an electron revolving in energy shells is given by:

$$m_e vr = nh / 2\pi$$

Where,
n = number of corresponding energy shell; 1, 2, 3 …..
m_e = mass of the electron
v = velocity
r = radius
h = Plank's constant

1.6.1 Defects (Limitation) of Bohr Atomic Model Theory

1. It violates the Heisenberg Uncertainty Principle. The Bohr atomic model theory considers electrons to have both a known radius and orbit i.e. known position and momentum at the same time, which is impossible according to Heisenberg.
2. The Bohr atomic model theory made correct predictions for smaller sized atoms like hydrogen, but poor spectral predictions are obtained when larger atoms are considered.
3. It failed to explain the Zeeman effect when the spectral line is split into several components in the presence of a magnetic field.
4. It failed to explain the Stark effect when the spectral line gets split up into fine lines in the presence of electric field.



1.7 COMPTON EFFECT

Compton effect is one of three principle forms of photon interaction. It is the main cause of scattered radiation in a material. It occurs due to the interaction of the X-ray or gamma photon with the outermost (and hence loosely bound) valence electron at the atomic level. The resultant incident photon gets scattered (changes direction) as well as ejects the electron (recoil electron), which further ionizes other atoms. Therefore the Compton effect is a partial absorption process and as the original photon has lost energy, this is known as Compton shift (the shift being a shift of wavelength/frequency).

Convincing evidence that light is made up of particles (photons), and that photons have momentum, can be seen when a photon with energy hf collides with a stationary electron. Some of the energy and momentum is transferred to the electron (this is known as the Compton effect), but both energy and momentum are conserved in this elastic collision. After the collision the photon has energy $hf^{/}$ and the electron has acquired a kinetic energy K.
Conservation of energy: $hf = hf^{/} + K$
Combining this with the momentum conservation equations, it can be shown that the wavelength of the outgoing photon is related to the wavelength of the incident photon by the equation:

$$\Delta\lambda = \lambda^{/} - \lambda = (h/m_ec)\,(1 - \cos\theta)$$

The combination of factors $h/m_ec = 2.43 \times 10^{-12}$ m, where m_e is the mass of the electron, is known as the Compton wavelength. The collision causes the photon wavelength to increase by somewhere between 0 (for a scattering angle of 0°) and twice the Compton wavelength (for a scattering angle of 180°).

1.8 DE BROGLIE’S HYPOTHESIS

In 1923, Louis de Broglie, a French physicist, proposed a hypothesis to explain the theory of the atomic structure. By using a series of substitution de Broglie hypothesizes particles to hold properties of waves. Within a few years, de Broglie's hypothesis was tested by scientists shooting electrons and rays of lights through slits. What scientists discovered was the electron stream acted the same was as light proving de Broglie correct.

The de Broglie wavelength is the wavelength, λ, associated with a object and is related to its momentum and mass. De Broglie derived his equation using well established theories through the following series of substitutions:

1. De Broglie first used Einstein's famous equation relating matter and energy:

$$E = mc^2$$

Where E = energy,
m = mass,
c = speed of light

2. Using Planck's theory which states every quantum of a wave has a discrete amount of energy given by Planck's equation:

$$E = h\nu$$

Where E = energy,
h = Plank's constant (6.62607 x 10^{-34} J s),
ν = frequency

3. Since de Broglie believed particles and wave have the same traits, he hypothesized that the two energies would be equal:

$$mc^2 = h\nu$$

4. Because real particles do not travel at the speed of light, De Broglie submitted velocity (v) for the speed of light (c).

$$mv^2 = h\nu$$

5. Through the equation λ, de Broglie substituted v/λ for ν and arrived at the final expression that relates wavelength and particle with speed.

$$mv^2=hv\lambda$$

Hence: $\lambda = hvmv^2 = hmv$

Although De Broglie was credited for his hypothesis, he had no actual experimental evidence for his conjecture. In 1927, Clinton J. Davisson and Lester H. Germer shot electron particles onto a Nickel crystal. What they saw was the diffraction of the electron similar to wave's diffraction against crystals (x-rays). In the same year, an English physicist, George P. Thomson fired electrons towards thin metal foil providing him with the same results as Davisson and Germer.

1.9 THE HEISENBERG UNCERTAINITY PRINCIPLE

Heisenberg’s Uncertainty Principle is one of the most celebrated results of quantum mechanics and states that one (often, but not always) cannot know all things about a particle (as it is defined by its wave function) at the same time. This principle is mathematically manifested as non-commuting operators.

Heisenberg's Uncertainty Principle states that there is inherent uncertainty in the act of measuring a variable of a particle. Commonly applied to the position and momentum of a particle, the principle states that the more precisely the position is known the more uncertain the momentum is and vice versa. This is contrary to classical Newtonian physics which holds all variables of particles to be measurable to an arbitrary uncertainty given good enough equipment. The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

More specifically, if one knows the precise momentum of the particle, it is impossible to know the precise position, and vice versa. This relationship also applies to energy and time, in that one cannot measure the precise energy of a system in a finite amount of time. Uncertainties in the products of “conjugate pairs” (momentum/position) and (energy/time) were defined by Heisenberg as having a minimum value corresponding to Planck’s constant divided by 4π.

More clearly:

$$\Delta p\Delta x \geq h4\pi$$

$$\Delta t\Delta E \geq h4\pi$$

Where Δ refers to the uncertainty in that variable and h is Planck's constant.

Aside from the mathematical definitions, one can make sense of this by imagining that the more carefully one tries to measure position, the more disruption there is to the system, resulting in changes in momentum. For example compare the effect that measuring the position has on the momentum of an electron versus a tennis ball. Let’s say to measure these objects, light is required in the form of photon particles. These photon particles have a measurable mass and velocity, and come into contact with the electron and tennis ball in order to achieve a value in their position. As two objects collide with their respective momenta (p=m*v), they impart these momenta onto each other. When the photon contacts the electron, a portion of its momentum is transferred and the electron will now move relative to this value depending on the ratio of their mass. The larger tennis ball when measured will have a transfer of momentum from the photons as well, but the effect will be lessened because its mass is several orders of magnitude larger than the photon. To give a more practical description, picture a tank and a bicycle colliding with one another, the tank portraying the tennis ball and the bicycle that of the photon. The sheer mass of the tank although it may be traveling at a much slower speed will increase its momentum much higher than that of the bicycle in effect forcing the bicycle in the opposite direction. The final result of measuring an object's position leads to a change in its momentum and vice versa.

All Quantum behaviour follows this principle and it is important in determining spectral line widths, as the uncertainty in energy of a system corresponds to a line width seen in regions of the light spectrum explored in Spectroscopy.

1.10 HAMILTONION OPERATOR

In quantum mechanics, the Hamiltonian is the operator corresponding to the total energy of the system in most of the cases. It is usually denoted by H, also $\check{H}$ or $\hat{H}$. Its spectrum is the set of possible outcomes when one measures the total energy of a system. Because of its close relation to the time-evolution of a system, it is of fundamental importance in most formulations of quantum theory.

The Hamiltonian is named after Sir William Rowan Hamilton (1805–1865), an Irish physicist, astronomer and mathematician, best known for his reformulation of Newtonian mechanics, now called Hamiltonian mechanics.

One particularly important operator in quantum mechanics is the Hamiltonian operator, H. The precise form of this operator varies according to the system under consideration, but in all cases it is the operator corresponding to the total energy of the system. i.e. if we can find a mathematical function that precisely describes the system of interest, then if it is an eigenfunction of the Hamiltonian operator, the eigenvalue of the function is equal to the total energy of the system:

$$\hat{H}\Psi = E\Psi$$

where Ψ is an eigen function that describes the system, and E is the total energy of the system.

Note that the above equation is a general form of a very important equation known as the Schrodinger equation. This equation is of great importance in quantum mechanics, because it provides a way of calculating the function Ψ.

We must write out the equation as above, substitute in the full form of the Hamiltonian operator for the system under consideration and then solve the equation to obtain Ψ. Examples of this procedure occur throughout quantum mechanics.

Since H is the operator corresponding to the total energy of the system, it should come as no surprise to learn that it is the sum of the operators corresponding to the kinetic and potential energies of the system.

1.11 STATEMENT OF THE BORN OPENHEIMER APPROXIMATION

In quantum chemistry and molecular physics, the **Born–Oppenheimer** (**BO**) **approximation** is the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. The approach is named after Max Born and J. Robert Oppenheimer. In mathematical terms, it allows the wavefunction of a molecule to be broken into its electronic and nuclear (vibrational, rotational) components.

The forces on both electrons and nuclei due to their electric charge are of the same order of magnitude, and so the changes which occur in their momenta as a result of these forces must also be the same. One might, therefore, assume that the actual momenta of the electrons and nuclei were of similar magnitude. In this case, since the nuclei are so much more massive than the electrons, they must accordingly have much smaller velocities. Thus it is plausible that on the typical time-scale of the nuclear motion, the electrons will very rapidly relax to the instantaneous ground-state configuration, so that in solving the time-independent Schrödinger equation resulting from the Hamiltonian in equation, we can assume that the nuclei are stationary and solve for the electronic ground-state first and then calculate the energy of the system in that configuration and solve for the nuclear motion. This separation of electronic and nuclear motion is known as the Born-Oppenheimer approximation.

Computation of the energy and the wavefunction of an average-size molecule is simplified by the approximation. For example, the benzene molecule consists of 12 nuclei and 42 electrons. The time independent Schrödinger equation, which must be solved to obtain the energy and wavefunction of this molecule, is a partial differential eigenvalue equation in 162 variables—the spatial coordinates of the electrons and the nuclei. The BO approximation makes it possible to compute the wavefunction in two less complicated consecutive steps. This approximation was proposed in 1927, in the early period of quantum mechanics, by Born and Oppenheimer and is still indispensable in quantum chemistry.

1.12 DEGREE OF FREEDOM

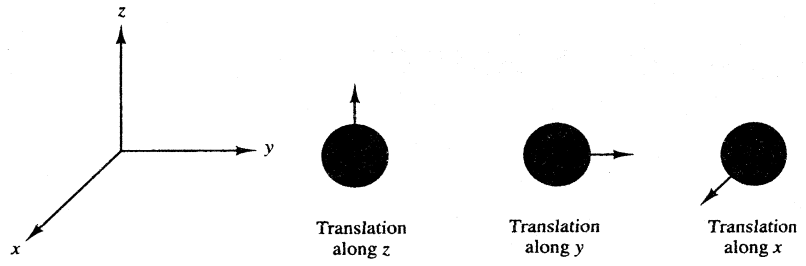
Degree-of-freedom of a general mechanical system is defined as the minimum number of independent variables required to describe its configuration completely. The set of variables (dependent or independent) used to describe a system are termed as the configuration variables. For a mechanism, these can be either Cartesian coordinates of certain points on the mechanism or the joint angles of the links or a combination of both. The set of configuration variables form what is known as the configuration space (denoted by C) of the mechanism.

In classical mechanics, the state of a point particle at any given time is often described with position and velocity coordinates in the Lagrangian formalism or with position and momentum coordinates in the Hamiltonian formalism.

In statistical mechanics, a degree of freedom is a single scalar number describing the microstate of a system. The specification of all microstates of a system is a point in the system's phase space.

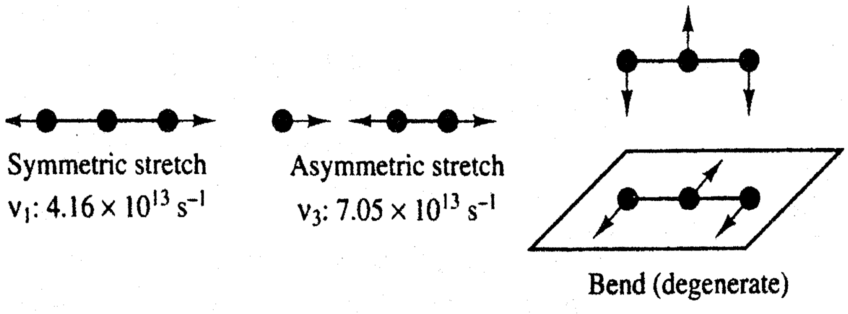
(A) One atom: In the context of molecular motion these are the spatial coordinates of all the particles. Since we need three coordinates to describe the position of an atom, we say the atom has three degrees of freedom.

(B) Diatomic molecule: If the atoms are not bound to one another, there will be no relation among the coordinates of the two atoms. On the other hand, when the two atoms are bound, the displacement of each other is coupled to the other. The result is to give three translational, one vibrational and two rotational degrees of freedom for the molecule. The vibrational and rotational degrees of freedom are also referred to as internal degrees of freedom.

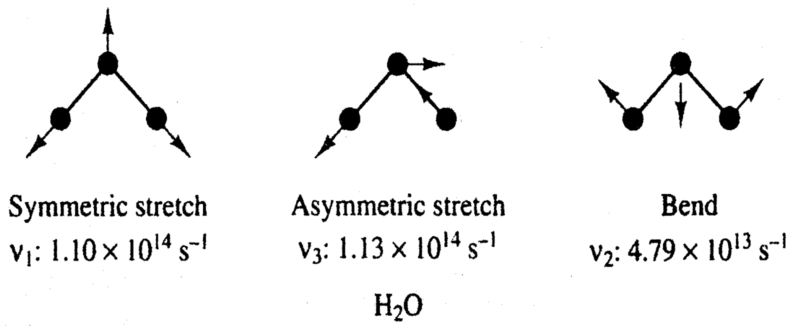


(C) Polyatomic molecule with N atoms:
   (i) Linear molecule: The 3N degrees of freedom of the atoms become three translational degrees of freedom and (3N-3) internal degrees of freedom. By analogy with diatomic molecules, we expect two rotational degrees of freedom for any linear polyatomic molecule (e.g. CO_2 and C_2H_2). The remaining (3N-5) internal coordinates must correspond to vibrations.
   (ii) Bent molecule: A bent molecule loses a vibrational degree of freedom while gaining a rotational degree of freedom. Therefore, a nonlinear polyatomic molecule has three rotational degrees of freedom, hence (3N-6) vibrational degrees of freedom.

e.g. vibrational motions for CO_2 and H_2O:



CO_2



H_2O

Bent polyatomic
3
3N-6
3

1.12.1 Degre

es of freedom of gas molecules

In three-dimensional space, three degrees of freedom are associated with the movement of a particle. A diatomic gas molecule thus has 6 degrees of freedom. This set may be decomposed in terms of translations, rotations, and vibrations of the molecule. The center of mass motion of the entire molecule accounts for 3 degrees of freedom. In addition, the molecule has two rotational degrees of motion and one vibrational mode. The rotations occur around the two axes perpendicular to the line between the two atoms. The rotation around the atom–atom bond is not a physical rotation. This yields, for a diatomic molecule, a decomposition of:

$$3N=6=3+2+1$$

For a general (non-linear) molecule with $N > 2$ atoms, all 3 rotational degrees of freedom are considered, resulting in the decomposition:

$$3N=3+3+(3N-6)$$

which means that an N-atom molecule has $3N-6$ vibrational degrees of freedom for $N>2$. In special cases, such as adsorbed large molecules, the rotational degrees of freedom can be limited to only one.

As defined above one can also count degrees of freedom using the minimum number of coordinates required to specify a position. This is done as follows:

1. For a single particle we need 2 coordinates in a 2-D plane to specify its position and 3 coordinates in 3-D space. Thus its degree of freedom in a 3-D space is 3.
2. For a body consisting of 2 particles (ex. a diatomic molecule) in a 3-D space with constant distance between them (let's say d) we can show (below) its degrees of freedom to be 5.

Let's say one particle in this body has coordinate (x_1, y_1, z_1) and the other has coordinate (x_2, y_2, z_2) with z_2 unknown. Application of the formula for distance between two coordinates

$$d = \sqrt{}(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2$$

results in one equation with one unknown, in which we can solve for z_2. One of x_1, x_2, y_1, y_2, z_1, or z_2 can be unknown.

Contrary to the classical equipartition theorem, at room temperature, the vibrational motion of molecules typically makes negligible contributions to the heat capacity. This is because these degrees of freedom are frozen because the spacing between the energy eigenvalues exceeds the energy corresponding to ambient temperatures ($k_B T$). In the following table such degrees of freedom are disregarded because of their low effect on total energy. However, at very high temperatures they cannot be neglected.

1.13 SUMMARY

In this unit we have given brief introduction on elementary quantum mechanics and described the black body radiation, explaining the laws of radiation, defining different effects involved in quantum mechanics like photoelectric effect, Compton effect, de broglie's hypothesis, Heisenberg's uncertainity principle, Bohr's model of Hydrogen atom, heat capacity of solids.

1.14 TERMINAL QUESTIONS

1. Calculate the de Broglie wavelength of a body of mass 1 mg moving with a velocity of 10 ms^{-1}.
2. Find the de Broglie wavelength for an electron moving at the speed of 5.0×10^6 m/s (mass of an electron is 9.1×10^{-31} kg).
3. An electron has kinetic energy 2.8x 10^{-25} J. Calculate its de Broglie's wavelength. $m_e = 9.1\times 10^{-31}$ kg.
4. Calculate the uncertainty in the velocity of an electron if the uncertainty in its position is approximately 1 Å.
5. Sirius, one of the hottest stars has a black body spectrum with λ_{max} = 2600 Å. Calculate its surface temperature.
6. Explain Born-Oppenheimer approximation and heat capacity of solids.

1.15 ANSWERS

1. 6.626×10^{-29} m
2. 1.46×10^{-10} m
3. 9.245×10^{-7} m
4. 5.8×10^5 ms-1
5. 1.1×10^4 K

UNIT 2: MOLECULAR STATISTICS

Structure

2.1 INTRODUCTION

Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties-spectra, rate constants etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice also be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

Statistical mechanics provides a link between quantum mechanics (or wave mechanics) and classical thermodynamics. Classical thermodynamics deals with macroscopic properties of matter and describes the behaviour of large number of molecules in terms of properties such as pressure, volume, temperature, composition, etc. Quantum mechanics on the other hand, deals almost exclusively with matter at the microscopic level. It tells us that each microscopic system can be described by wave function. However, it does not indicate which wave function of a molecule from, say, an Avogadro's number of molecules constituting a system, will represent the state of the system at a given instant. Neither classical thermodynamics nor quantum mechanics is able to calculate the macroscopic properties of matter from the microscopic structures of individual molecules.

Statistical mechanics can be applied easily to simple, ideal systems such as monoatomic and diatomic gases. For application to interesting systems such as liquids (where strong intermolecular forces exist), the details of the intermolecular potential energy, which is not always known accurately, have also to be taken in account. That is why statistical mechanics of liquids is a difficult but fascinating subject. Gases under high pressure, too are difficult to treat statistically since they deviate strongly from ideality. In recent years statistical methods have been applied successfully to simple liquids and dense gases. Progress in the area has been made possible by the application of both the advanced mathematical methods and high sped computers, which can numerically solve the otherwise highly intractable differential and integro-differential equations involved in advanced theoretical treatments.

Since any observed equilibrium property of matter must be some kind of an average of a large number of molecules, it is evident that we must use statistical method to determine this property. The discipline which deals with the computation of the macroscopic properties of matter from the data on the microscopic properties of individual atoms (or molecules) is called statistical mechanics or statistical thermodynamics.

This unit deals with the molecular statistics, a modern alternative of the classical (phenomenological) thermodynamics. Its aim is to determine thermodynamic properties of matter from forces acting among molecules. Roots of the discipline are in kinetic theory of gases and are connected with the names Maxwell and Boltzmann. Father of the statistical thermodynamics is Gibbs who introduced its concepts such as the statistical ensemble and others, that have been used up to present.

In chemistry, we are concerned with a collection of molecules. If the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system.

Objectives

After studying this unit, you should be able to

- know about molecular statistics
- to understand the Boltzman distribution
- describe Maxwell distribution law for distribution of molecular speeds and energies
- define partition function and thermodynamic quantities from partition functions
- explain Sackur-Tetrode equation for molar entropy of monatomic gases

2.2 THE BOLTZMANN DISTRIBUTION

1. The populations of energy levels:

Since any molecule can only posses certain energies at a given temperature, each of molecules can distribute over all the available energy levels. Although we cannot keep track of the energy state of a single molecule, we can speak of the average numbers of molecules in each state, and these average numbers are constant in time so long as the temperature remains the same. The average number of molecules in a state is called the population of the state. Only the lowest energy level is occupied at T = 0 K.

Raising the temperature excites some molecules into higher energy levels, and more and more levels become accessible as the temperature is raised further. Nevertheless, whatever the temperature, there is always a higher population in a state of low energy than one of high energy.

2. Boltzmann distribution:

The population in state *n* with energy E_n is determined by the temperature *T* according to the Boltzmann distribution:

This formula was derived by Ludwig Boltzmann towards the end of the 19th century. According to this

$$N_n = N_0 e^{-\frac{E_n}{k_B T}}$$

formula, the

population ratio of the numbers of particles in various states with energies E_i and E_j is determined by

The fundamental constant k_B is called Boltzmann's constant,

$$\frac{N_i}{N_j} = e^{-\frac{(E_i - E_j)}{k_B T}}$$

$$k_B = 1.38 \times 10^{-23}\, J/K$$

. Boltzmann’s constant is replaced by the gas constant, $R=N_Ak_B$, if the energies in the Boltzmann distribution are replaced by molar energies. The possibility f_i of molecules occupying the i-th state is

$$f_i = \frac{N_i}{N} = \frac{N_i}{\sum N_i} = \frac{e^{-\frac{E_i}{k_BT}}}{\sum e^{-\frac{E_i}{k_BT}}}$$

determined to be

$$f_i = \frac{N_i}{N} = \frac{N_i}{\sum N_i} = \frac{g_i e^{-\frac{E_i}{k_BT}}}{\sum g_i e^{-\frac{E_i}{k_BT}}}$$

In consideration of degeneracy, the equation is rewrriten to be:

The sum in the denominator is called the partition function, which means as “sum over states”.

The Boltzmann distribution law is written as

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-\frac{(E_i - E_j)}{k_BT}}$$

If f_i are the fractions of molecules in different quantum states, the average energy per particle $<E>$ is given by

$$\langle E \rangle = \sum f_i E_i$$

2.3 MAXWELL BOLTZMANN DISTRIBUTION LAW FOR THE DISTRIBUTION OF MOLECULAR SPEEDS

The Maxwell-Boltzmann equation, which forms the basis of the kinetic theory of gases, defines the distribution of speeds for a gas at a certain temperature. From this distribution function, the most probable speed, the average speed and the root-mean-square speed can be derived.

The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, the Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities *v* and *v* + *dv*. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the *y* and *z* directions does not affect the *x* velocity, for example, the Maxwell-Boltzmann distribution is given by

$$dN / N = (m / 2\pi k_B T)^{1/2} e^{-mv2 / 2kBT} dv$$

where

- dN/N is the fraction of molecules moving at velocity *v* to *v*+*dv*,
- m is the mass of the molecule,
- k_b is the Boltzmann constant, and
- T is the absolute temperature

Additionally, the function can be written in terms of the scalar quantity speed *c* instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between c_1 and c_2, thus

$$f(c) = 4\pi c^2 (m / 2\pi k_B T)^{3/2} e^{-mc^2 / 2k_B T}$$

Finally, the Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.

2.3.1 Plotting the Maxwell-Boltzmann Distribution Function

Figure 1 shows the Maxwell-Boltzmann distribution of speeds for a certain gas at a certain temperature, such as nitrogen at 298 K. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

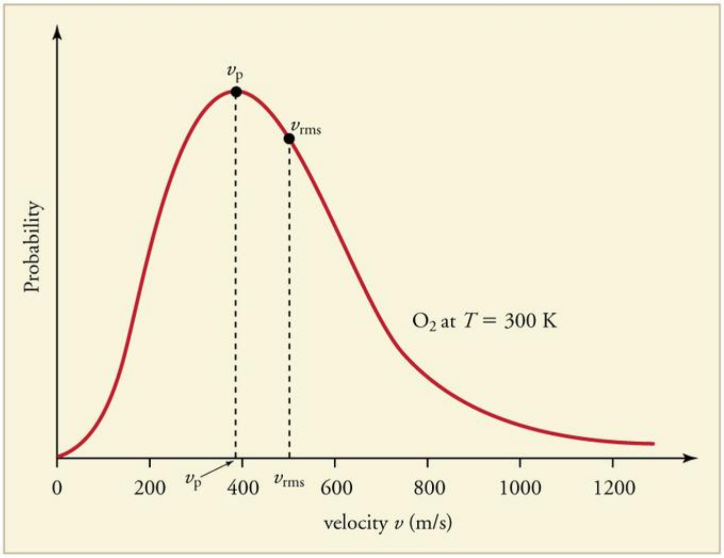


Figure 1: The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures

Figure 2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

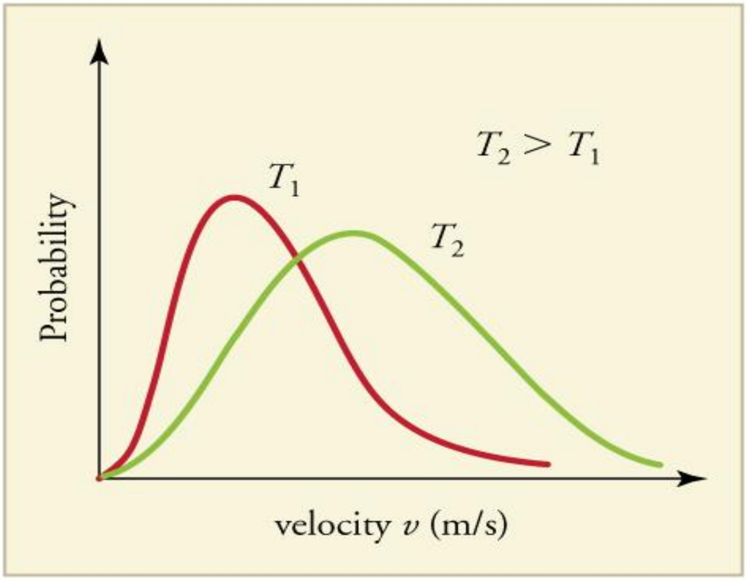


Figure 2: The Maxwell-Boltzmann distribution is shifted to higher speeds and

is broadened at higher temperatures

Figure 3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

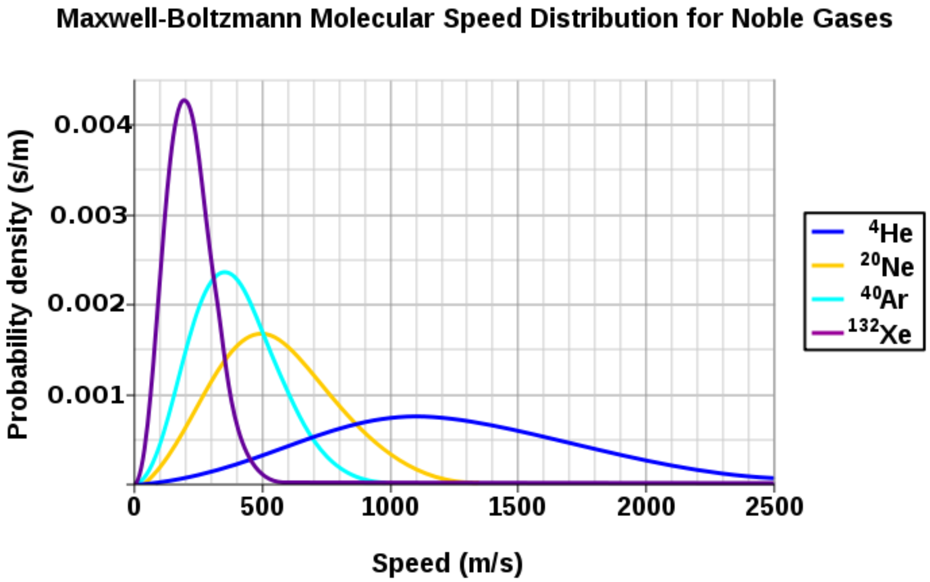


Figure 3*:* The speed probability density functions of the speeds of a few noble gases at a temperature of 298.15 K (25 °C). The y-axis is in s/m so that the area under any section of the curve (which represents the probability of the speed being in that range) is dimensionless.

2.3.2 Related Speed Expressions

Three speed expressions can be derived from the Maxwell-Boltzmann distribution: the most probable speed, the average speed, and the root-mean-square speed. The most probable speed is the maximum value on the distribution plot. This is established by finding the velocity when the following derivative is zero

$$df(c) / dc \setminus C_{mp} = 0$$

which is

$$C_{mp} = \sqrt{}2RT / M$$

The average speed is the sum of the speeds of all the molecules divided by the number of molecules.

$$C_{avg} = \int_0^{\infty} c f\,(c)\ dc = 8RT / \pi M$$

The root-mean-square speed is square root of the average speed-squared.

$$C_{rms} = 3RTM$$

where

- R is the gas constant
- T is the absolute temperature and
- M is the molar mass of the gas.

It always follows that for gases that follow the Maxwell-Boltzmann distribution (if thermallized)

$$C_{mp} < C_{avg} < C_{rms}$$

2.4 THE MAXWELL BOLTZMANN DISTRIBUTION LAW FOR THE DISTRIBUTION OF MOLECULAR ENERGIES

Maxwell-Boltzmann distribution law, a description of the statistical distribution of the energies of the molecules of a classical gas. This distribution was first set forth by the Scottish physicist James Clerk Maxwell in 1859, on the basis of probabilistic arguments, and gave the distribution of velocities among the molecules of a gas. Maxwell's finding was generalized (1871) by a German physicist, Ludwig Boltzmann, to express the distribution of energies among the molecules.

The distribution function for a gas obeying Maxwell-Boltzmann statistics ($f_{M–B}$) can be written in terms of the total energy (E) of the system of particles described by the distribution, the absolute temperature (T) of the gas, the Boltzmann constant ($k = 1.38\times10^{-16}$ erg per kelvin) and a normalizing constant (C) chosen so that the sum or integral, of all probabilities is unity *i.e.*, $f_{M–B} = Ce^{-E/kT}$, in which e is the base of the natural logarithms. The distribution function implies that the probability dP that any individual molecule has an energy between E and $E + dE$ is given by $dP = f_{M–B}\ dE$. The total energy (E) usually is composed of several individual parts, each corresponding to a different degree of freedom of the system. In fact, the total energy is divided equally between these modes.

The law can be derived in several ways, none of which is absolutely rigorous. All systems observed to date appear to obey Maxwell-Boltzmann statistics provided that quantum-mechanical effects are not important.

2.5 THE PARTITION FUNCTION

The partition function comes from a way of counting the particles of a system when the particles are distributed over the available energy levels in accord with the Boltzmann distribution.

Partition functions describe the statistical properties of a system in thermodynamic equilibrium. It is a function of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

The way to count the particles

The number of particles is to be counted as follows: First, represent the total number of particles by N. Then represent the number in the lowest energy level, or ground state, by n_0, represent the number in the first excited state by n_1, the number in the second excited state by n_2, and so on. Then represent the total number of particles, N, as the sum of the numbers in each energy level:

$$N = n_0 + n_1 + n_2 + n_3 + n_4 \,..... \qquad \text{Eq. 1}$$

In the Boltzmann distribution the number of particles in the first excited state is a fraction of the number of particles in the ground state, and that fraction is $(1/e^{\varepsilon_1/kT})$, where ε_1 is the energy of the first excited state, relative to the ground state, k is Boltzmann's constant, and T is the absolute temperature. Represent the number of particles in the first excited state as n_0 times this fraction: $n_0\,(1/e^{\varepsilon_1/kT})$.

The number of particles in the second excited state is also a fraction of the number of particles in the ground state, and this second fraction is $1/e^{\varepsilon_2/kT}$. This second fraction, however, is smaller than the first fraction because ε_2 is greater than ε_1. Represent the number of particles in the second excited state as n_0 times this second fraction: $n_0(1/e^{\varepsilon_2/kT})$. Continue in this way and then substitute the resulting expressions for the numbers of particles in each state into Eq. 1 to form Eq. 2.

$$N = n_0 + n_0(1/e^{\varepsilon_1/kT}) + n_0(1/e^{\varepsilon_2/kT}) + n_0(1/e^{\varepsilon_3/kT}) + n_0(1/e^{\varepsilon_4/kT})..... \text{ Eq. 2}$$

Next, factor out n_0 to give Eq. 3.

$$N = n_0\,(1 + 1/e^{\varepsilon_1/kT} + 1/e^{\varepsilon_2/kT} + 1/e^{\varepsilon_3/kT} + 1/e^{\varepsilon_4/kT}\ ) \;.... \qquad \text{Eq. 3}$$

Finally, divide both sides of equation 3 by n_0 to convert it to Eq. 4.

$$N / n_0 = 1 + 1/e^{\varepsilon_1/kT} + 1/e^{\varepsilon_2/kT} + 1/e^{\varepsilon_3/kT} + 1/e^{\varepsilon_4/kT} \quad .... \qquad \text{Eq. 4}$$

The sum of terms on the right of Eq. 4 is called the partition function.

When you let Q stand for the partition function you can rewrite Eq. 4 in a very concise form, as Eq. 5.

$$N / n_0 = Q \qquad .... \qquad \text{Eq. 5}$$

The partition function is thus seen to be the ratio of the total number of particles to the number of particles in the ground state. The partition function is the number of times larger the total number of particles is than the number of particles in the ground state. The partition function is a measure of the degree to which the particles are spread out over or partitioned among, the energy levels.

The partition function can also be seen to be the total number of particles expressed as the sum of the numbers of particles of each energy, with the population of the ground state being the unit of measure of population.

$$Q = 1 + 1/e^{\varepsilon_1/kT} + 1/e^{\varepsilon_2/kT} + 1/e^{\varepsilon_3/kT} + 1/e^{\varepsilon_4/kT} \;..... \text{Eq. 6}$$

The population of the ground state (the most highly populated state) is taken to be 1, and the populations of the other energy states are expressed as fractions of the population of the ground state. Considered in this way the partition function can be seen as a sum of the relative occupancies of states. It is for this reason that the partition function is also called the sum-overstates or Zustandsumme.

2.6 THERMODYNAMIC QUANTITIES FOR PARTITION FUNCTION

If the partition function is known thermodynamic quantities may be determined. The following relations between the partition function in the canonical ensemble and thermodynamic quantities can be derived

$$A = - k_B T \ln Q$$

$$U = k_B T^2 (\partial \ln Q/\partial T)_V$$

$$S = k_B \ln Q + k_B T (\partial \ln /\partial T)_V$$

$$C_V = (\partial U/\partial T)_V = k_B T^2 (\partial^2 \ln Q/ \partial T^2) + 2k_B T (\partial \ln Q/ \partial T)_V$$

$$p = -(\partial A/\partial V)_T = k_B T (\partial \ln Q/\partial V)_T$$

$$H = U + pV = k_B T^2 (\partial \ln Q/\partial T)_V + V k_B T (\partial \ln Q/\partial V)_T$$

$$G = A + pV = -k_B T \ln Q + V k_B T (\partial \ln Q/\partial V)_T$$

$$C_p = (\partial H/\partial T)_V = C_V + V k_B (\partial^2 \ln Q/\partial V \partial T)$$

A is Helmholtz free energy, U internal energy, S entropy, C_V isochoric heat capacity, p pressure, H enthalpy, G Gibbs free energy and C_p isobaric heat capacity.

2.7 THE SACKUR TETRODE EQUATION FOR MOLAR ENTROPY OF MONOATOMIC GASES

Sackur–Tetrode equation is an expression for the entropy of a monatomic classical ideal gas which incorporates quantum considerations which give a more detailed description of its regime of validity. The Sackur–Tetrode equation is named for Hugo Martin Tetrode (1895–1931) and Otto Sackur (1880–1914), who developed it independently as a solution of Boltzmann's gas statistics and entropy equations, at about the same time in 1912.

Statistical mechanical theory applied to spectroscopic measurements provides an accurate means of evaluating the molar entropy of a pure ideal gas from experimental molecular properties. This is often the preferred method of evaluating S_{m} for a gas. The zero of entropy is the same as the practical entropy scale-that is, isotope mixing and nuclear spin interactions are ignored. Intermolecular interactions are also ignored, which is why the results apply only to an ideal gas.

The statistical mechanics formula writes the molar entropy as the sum of a translational contribution and an internal contribution: $S_{\mathrm{m}} = S_{\mathrm{m,trans}} + S_{\mathrm{m,int}}$. The translational contribution is given by the Sackur–Tetrode equation:

$$S_{\mathrm{m,trans}} = R \ln(2\pi M)^{3/2}(RT)^{5/2} / ph^3 N^4_{\mathrm{A}} + (5/2)\, R$$

Here h is the Planck constant and N_{A} is the Avogadro constant. The internal contribution is given by

$$S_{\mathrm{m,int}} = R \ln q_{\mathrm{int}} + RT\, (\mathrm{d}\ln q_{\mathrm{int}} / \mathrm{d}T)$$

where q_{int} is the molecular partition function defined by

$$q_{\mathrm{int}} = \textstyle\sum_i \exp\,(-\epsilon_i / kT)$$

In the above equation, ϵ_i is the energy of a molecular quantum state relative to the lowest energy level, k is the Boltzmann constant, and the sum is over the quantum states of one molecule with appropriate averaging for natural isotopic abundance. The experimental data needed to evaluate q_{int} consist of the energies of low-lying electronic energy levels, values of electronic degeneracies, fundamental vibrational frequencies, rotational constants, and other spectroscopic parameters.

When the spectroscopic method is used to evaluate S_{m} with p set equal to the standard pressure $p_{\circ}$=1bar, the value is the standard molar entropy, $S_{\circ\mathrm{m}}$, of the substance in the gas phase. This value is useful for thermodynamic calculations even if the substance is not an ideal gas at the standard pressure.

2.8 ROTATIONAL AND VIBRATIONAL PARTITION FUNCTION

The electronic energy levels are generally very widely separated in energy compared to the thermal energy kT at room temperature. In each electronic level, there are several vibrational levels and for each vibrational level, there are several rotational states. This is a simplified and useful model to start with. The total energy is a sum of all these energies and is given by

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} + E_{others}$$

The term E_{others} includes nuclear spin energy levels and may also be used later to include the interactions between the first four. Assuming the first three to be independent and neglecting the last term, the molecular partition function (i.e., a sum over the molecular energy states) is given

$$q = \sum e^{-(Eel + Evib + Erot + Etrans)/k T} = \sum_{el} e^{-\beta E_{el}} \sum_{vib} e^{-\beta Evib} \sum_{rot} e^{-\beta E_{trans}} \sum_{trans} e^{-\beta Etrans}$$

Here, the summation is over the electronic, vibrational and rotational states can be done separately since they are assumed to be independent. Therefore,

$$q = q_{el}\, q_{vib}\, q_{rot}\, q_{trans}$$

The molecular partition q function is written as the product of electronic, vibrational, rotational and partition functions.

The partition function is a sum over states (of course with the Boltzmann factor b multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy. Since $E_{el} > E_{vib} > E_{rot} > E_{trans}$, there are far too many translational states available compared to the rotational, vibrational and electronic states. q_{el} is very nearly unity, q_{vib} and q_{rot} are in the range of 1 to 100 while q_{trans} can be much in excess of 10^{20}. We shall calculate the values of these qs and indicate how these qs are useful in calculating the equilibrium constants and also in certain cases, the rate constants.

Using the standard formulae for the translational, rotational and vibrational energy levels, we will now calculate the molecular translational, vibrational and rotational partition functions for diatomic molecules first.

2.8.1 The Translational Partition Function, q_{tr}.

Consider a molecule confined to a cubic box. A molecule inside a cubic box of length L has the translational energy levels given by $E_{tr} = h^2 (n_x^2 + n_y^2 + n_z^2) / 8 mL^2$ where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by

$$\sum_{trans} e^{-\beta Etrans} = \sum_X e^{-\beta E_x} \sum_y e^{-\beta Ey} \sum_z e^{-\beta Ez}$$

$$q_{tr} = q_x \, q_y \, q_z$$

which is the product of translational partition functions in the three directions. Since the levels are very closely spaced, we can replace the sum by an integral

$$q_x = \int_1^\infty e^{-n_x^2 h^2 / (8mL^2 k_B t)} \, dnx \approx \int_1^\infty e^{-an_x^2} \, dnx \;, \; a = h^2/8mL^2 k_B t$$

using $\int_1^\infty e^{-ax^2} dx = ½ \sqrt{\pi} / a$ we get,

$$q_x = ½ \sqrt{\pi} / a = ½ \sqrt{8\pi m k_B T} / h \,.\, L = \sqrt{2\pi m k_B T} / h \,.\, L = L/\Lambda$$

where, Λ is the de Broglie thermal wavelength given by $h / \sqrt{2\pi m k_B T}$.

Multipying q_x, q_y and q_z, and using V = volume of the box = L^3, we have,

$$q_{tr} = [\ 2\pi mkBT / h^2\ ]^{3/2}\ V = V / \Lambda^3$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for a typical small molecular mass. This means that such a large number of translational states are accessible or available for occupation by the molecules of a gas.

2.8.2 The Rotational Partition Function of a Diatomic

The rotational energy levels of a diatomic molecule are given by

$$E_{rot} = \bar{B}\ J(J + 1) \text{ where } \bar{B} = h / 8\ \pi^2 Ic$$

Here, $\bar{B}$ is the rotational constant expresses in cm^{-1}. The rotational energy levels are given by $\varepsilon_J = J\ (J + 1)\ h^2 / 8\ \pi^2 I$, where I is the moment of inertia of the molecule given by μr^2 where, μ is the reduced mass and r, the bond length. Often, the energies are also expressed in terms of the rotational temperature, Θ_r or Θ_{rot}, which is defined as

$$\Theta_r = h^2 / 8\ \pi^2\ Ik$$

In the summation for the expression for q_{rot}, we can do an explicit summation

$$q_{rot} = \sum_J (2J + 1)\ e^{-E_{rot,\,J} / kT}$$

if only a few terms contribute. The factor (2J+1) for each term accounts for the

degeneracy of a rotational state J. If energy E_J is degenerate with (2J+1) states corresponding to it, then, the Boltzmann factor $e^{-E_{rot,j} / k_B T}$ has to be multiplied by (2J+1) to account for all these states. If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} above to get

$$q_{rot} = \int_0^{\infty} (2J + 1)\ e^{-\bar{B}J(J+1) / kT} dJ$$

the integration can be easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)\, dJ$

$$q_{rot} = kT / B$$

For a homonuclear diatomic molecule, rotating the molecule by 180º brings the molecule into a configuration which is indistinguishable from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the symmetry number, which is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes,

$$q_{rot} = kT / \sigma \bar{B}$$

2.8.3 The Vibrational Partition Function of a Diatomic

The vibrational energy levels of a diatomic are given by

$$E_n = (n + ½)\, h\nu$$

where is n the vibrational frequency and n is the vibrational quantum number.

In this case, it is easy to sum the geometric series shown below

$$q_{vib} = \sum_{n=0}^{\infty} e^{-(n + ½)\, h\nu / kT}$$

$$= e^{- h\nu / (2k_B T)} (1 + e^{- h\nu / k_B T} + e^{-2h\nu / k_B T} \ldots\ldots)$$

$$= e^{- h\nu / 2kT} (1 + x + x^2 + \ldots\ldots)$$

$$= e^{-h\nu / 2kT} [1 / 1-x]$$

where $x = e^{-h\nu / k_B T}$ which is less than 1. Threfore,

$$q_{vib} = e^{-h\nu / 2kT} / 1- e^{-h\nu / kT}$$

$$q_{vib} = 1 / 1- e^{-h\nu / kT}$$

if the zero of energy scale is at hν/2kT. Analogous to Θ_r, a vibrational temperature Θ_v or q_{vib} may be defined as hcν /k, where, ν is the vibrational frequency in cm^{-1}.

2.8.4 The Electronic Partition Function

Writing the electronic energy as E_1, E_2, E_3,…with degeneracies g_1, g_2, g_3,…the electronic partition function is given by

$$q_{el} = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3}$$

Usually, $E_1 << E_2$ or E_3. Treating E_1 to be the reference value of zero of energy, we get,

$$q_{el} = g_1$$

which is the ground state degeneracy of the system.

2.9 THE CHARACTERISTIC TEMPERATURE

2.9.1 Characteristic rotational temperature (θ_R or θ_{rot})

The characteristic rotational temperature (θ_R or θ_{rot}) is commonly used in statistical thermodynamics, to simplify the expression of the rotational partition function and the rotational contribution to molecular thermodynamic properties. It has units of temperature and is defined as,

$$\theta_R = hc\bar{B} / k_B = h^2 / 2k_BI$$

where $\bar{B}$= B / hc is the rotational constant, and I is a molecular moment of inertia. Also h is the Planck constant, c is the speed of light, ħ = h/2π is the reduced Planck constant and k_B is the Boltzmann constant.

The physical meaning of θ_R is as an estimate of the temperature at which thermal energy (of the order of k_BT) is comparable to the spacing between rotational energy levels (of the order of hcB). At about this temperature the population of excited rotational levels becomes important. Some typical values are given in the table. In each case the value refers to the most common isotopic species.

2.9.2 Characteristic vibrational temperature (θ_{vib})

The vibrational temperature is commonly used in thermodynamics, to simplify certain equations. It has units of temperature and is defined as

$$\theta_{vib} = h\nu / k_B$$

where k_B is Boltzmann's constant.

The vibrational temperature is used commonly when finding the vibrational partition function.

2.10 THE CALCULATION OF GIBBS FREE ENERGY CHANGES AND EQUILIBRIUM CONSTANT IN TERMS OF PARTITION FUNCTION

For an ideal gas,

$$G = A + PV = A + RT \qquad (1)$$

Since $$A= -RT\ln (q/N_A) - RT \qquad (2)$$

$$G = -RT \ln (q^o/N_A) \qquad (3)$$

Hence, the standard molar Gibbs function is given by

$$G = -RT\ln (q^o/N_A) \qquad (4)$$

Where q^o is the molecular partition function for a gas at standard pressure which may be represented as

$$q^o = q_0\ q^o_{tr}\ q^o_{rot}\ q^o_{vib}\ q^o_{elec}\ q^o_{nucl} \qquad (5)$$

Here q^o is the zero-point energy term defined as

$$q^o = e^{-\varepsilon^o/kT} \qquad (6)$$

$$q^o_{tr} = (2\pi mkT/h^2)^{3/2} \times V^o \qquad (7)$$

where V^o is the molar volume at pressure P^oIf we represent the new partition function q' as

$$q` = q_0\ q^o_{tr}\ q^o_{rot}\ q^o_{vib}\ q^o_{elec}\ q^o_{nucl} \qquad (8)$$

we obtain $$q^o = q_0\, q` = q`\, e^{-\varepsilon^o/kT} \qquad (9)$$

Let us consider a reaction

$$aA + bB = cC + dD \qquad (10)$$

In order to calculate the equilibrium constant of this reaction we have to calculate the partition function of the reactant and product species relative to the same zero energy. For the reaction A↔B, the energy levels for A and B molecules are shown in figure 4.

In practise, of course, it is more convenient to compute the partition function of each species relative to its own ground energy level, setting the each ground level to zero. Thus, relative to arbitrary zero, the lowest energy of A, B, C and D are ε_{0A}, ε_{0B}, ε_{0C}, ε_{0D} respectively.

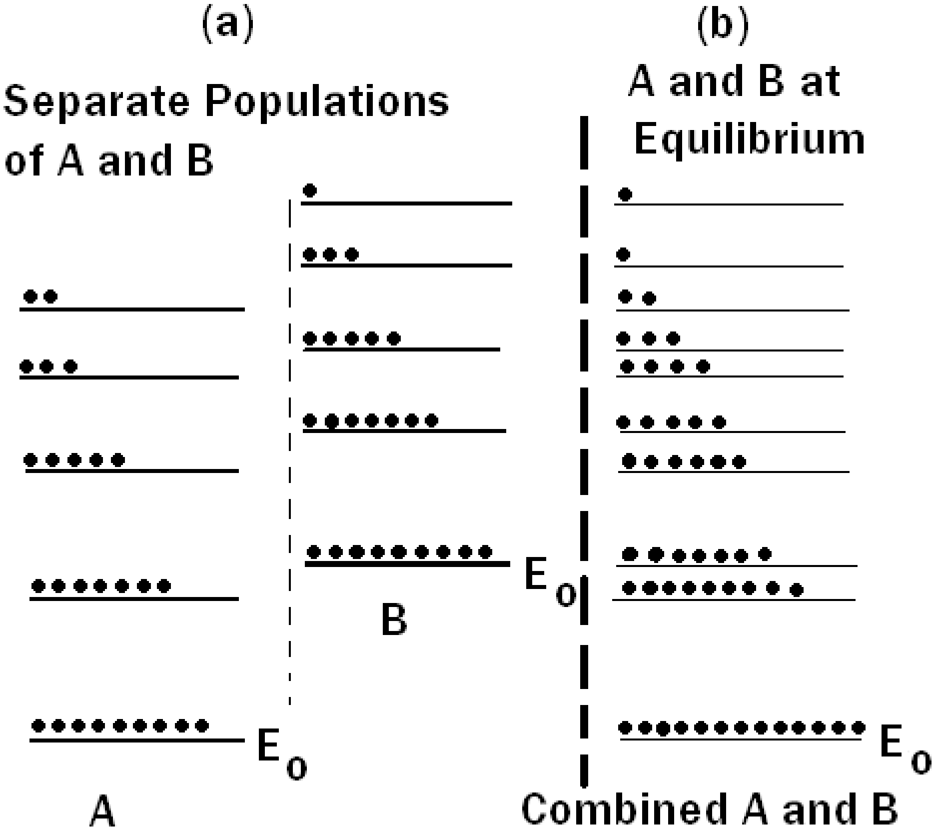


Figure 4 (a) Energy levels of individual molecules A, B and the individual populations of these levels, (b) Energy levels of the combined system A and B and the relative populations of the combined levels at equilibrium (schematic).

The standard Gibbs free energy change for the reaction is given by

$$\Delta G^o = (cG^o_C + dG^o_D) - (aG^o_A + bG^o_B) \qquad (11)$$

Using Eqs. 11 and 4,

$$\Delta G^o = -RT\,[\{c \ln q`_C/N + d \ln q`_D/N\}-\{a \ln q`_A/N + b \ln q`_B/N\}- c\,\varepsilon_{0C} + d\,\varepsilon_{0D} - a\,\varepsilon_{0A} - b\,\varepsilon_{0B}/ kT]$$

$$= RT\,[(c \ln q`_C + d \ln q`_D) - (a \ln q`_A + b \ln q`_B) + \ln (1/N)^{\Delta\nu} - (\Delta\varepsilon_0 /kT)] \qquad (12)$$

Where $\Delta\nu$ is the change in the number of molecules represented in the stoichiometric equation, i.e.

$$\Delta\nu = (c + d) + (a + b) \qquad (13)$$

And $$\Delta\varepsilon_0 = (c\varepsilon_{0C} + d\varepsilon_{0D}) + (a\varepsilon_{0A} + b\varepsilon_{0B}) \qquad (14)$$

Hence, $$\Delta G^o = - RT\,[\ln\{(q`_C)^c (q`_D)^d / (q`_A)^a (q`_B)^b \;(1/N)^{\Delta\nu}\}- \Delta\varepsilon_0 /kT\,] \qquad (15)$$

Since from the van’t Hoff isotherm,

$$\Delta G^o = - RT \ln K_p \qquad (16)$$

where K_p is the equilibrium constant of the reaction in terms of partial pressure, we obtain

$$K_p = (q`_C)^c (q`_D)^d / (q`_A)^a (q`_B)^b \;(1/N)^{\Delta\nu}\, e^{-\varepsilon^o/kT} \qquad (17)$$

2.11 SUMMARY

In this unit you have studied about the brief introduction of the statistical mechanics, explained Boltzmann distribution, described in detail about the Maxwell-Boltzmann distribution law for the distribution of molecular speeds and molecular energies, defined the partition functions and derived thermodynamic quantities from partition functions. We have explained the Sackur-Tetrode equation for molar entropy of monatomic gases, know about rotational and vibrational partition functions, the characteristic temperature and calculate Gibbs free energy changes and equilibrium constant in terms of partition functions.

2.12 TERMINAL QUESTIONS

1. Using the Sackur-tetrode equation, calculate the (translational entropies of the inert gases He, Ne Ar, Kr , Xn, Rn at 298.15 K at 1 atm pressure (101.32 kPa) comment on your result.
   [Hint: On numerical substitution of the various constants, the Sackur –Tetrode equation becomes:

   Sm= 195 + (3/2) R ln M($JK^{-1}mol^{-1}$) where M is the molar mass in Kg.]

2. For CO, Θ_{rot} = 2.77 K and Θ_{vib} = 3084 K. For one mole of this gas at 25ºC and 1 atm pressure calculate the translational, rotational, vibrational and electronic partition functions.
3. Calculate the translational partition unction of for Hydrogen atom at 1000 K and 1 atm.
4. The fundamental vibrational frequency of F_2 is 2.676×10^{13} Hz. Calculate the vibrational partition function of F_2 at 25ºC.
5. Calculate the rotational partition unction for the O-H radical at 27ºC, given that the bond length r (O-H)= 0.971Å.
6. Calculate the rotational partition unction for F_2 at 25ºC, given that I= 32.5×10^{-47} kg m^2.

2.13 ANSWERS

1. 126, 146,155,164,170,176 $JK^{-1}mol^{-1}$
2. $q_{tr} = 3.51\times10^{30}$, $q_{rot} = 108$, $q_{vib} = 1.000032$, $q_{el} = 1$
3. 4.94×10^{29}
4. 0.1177
5. 11.05
6. 120

UNIT 3: LAWS OF PHOTOCHEMISTRY

Structure

3.1 INTRODUCTION

Photochemistry is the branch of chemistry that deals with the chemical processes that are caused by the absorption of light energy. The process by which a photochemical reaction is carried out is called photolysis. Photolysis is usually initiated by infrared, visible, or ultraviolet light. A primary photochemical reaction is the immediate consequence of the absorption of light. Subsequent chemical changes are called secondary processes.

Photochemical reactions are utilized in synthetic chemistry to produce various organic molecules. In addition, many common processes are photochemical in nature and have important applications. For example: Photosynthesis involves the absorption of light by the chlorophyll in plants to produce carbohydrates from carbon dioxide and water. Photography uses the action of light on grains of silver chloride or silver bromide to produce an image. Ozone formation in the upper atmosphere results from action of light on oxygen molecules.

Solar cells, which are used to power satellites and space vehicles, convert light energy from the sun to chemical energy and then release that energy in the form of electrical energy.

Photochemical reactions are of great importance for the life on Earth. Chemical changes taking place in the atmospheric gases of the earth are initiated by radiations and modified by the suspended particles. These are very useful for the support of life. The study of upper atmospheric photochemical reaction have significantly contributed to the knowledge of depletion of ozone layer, acid rain and global warming.

3.1.1 Interaction of radiation with matter

The detection, characterization and effects of radiation are almost entirely dependent upon their interaction with matter.

Types of radiation are direct ionizing radiation and indirect ionizing radiation. The flows of charged particles, such as alpha particles, beta particles, electrons, are phenomena of direct ionizing radiation, because through coulomb interaction with matter it directly causes ionization and excitation of atoms. Indirect ionizing radiation (neutrons, γ-quantums) is radiation of particles or photons, which have no charge and during interaction with matter can transfer energy to charged particles, nuclei and atom electrons due to electromagnetic or nuclear interaction.

It is well known that all matter is comprised of atoms. But subatomically, matter is made up of mostly empty space. For example, consider the hydrogen atom with its one proton, one neutron, and one electron. The diameter of a single proton has been measured to be about 10^{-15} meters. The diameter of a single hydrogen atom has been determined to be 10^{-10} meters, therefore the ratio of the size of a hydrogen atom to the size of the proton is 100,000:1. Consider this in terms of something more easily pictured in your mind. If the nucleus of the atom could be enlarged to the size of a softball (about 10 cm), its electron would be approximately 10 kilometers away.

Therefore, when electromagnetic waves pass through a material, they are primarily moving through free space, but may have a chance encounter with the nucleus or an electron of an atom.

Because the encounters of photons with atom particles are by chance, a given photon has a finite probability of passing completely through the medium it is traversing. The probability that a photon will pass completely through a medium depends on numerous factors including the photon's energy and the medium's composition and thickness. The more densely packed a medium's atoms, the more likely the photon will encounter an atomic particle. In other words, the more subatomic particles in a material (higher Z number), the greater the likelihood that interactions will occur Similarly, the more material a photon must cross through, the more likely the chance of an encounter.

When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be re-emitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material. Let us first consider the interaction of visible light. Reflection and transmission of light waves occur because the light waves transfer energy to the electrons of the material and cause them to vibrate. If the material is transparent, then the vibrations of the electrons are passed on to neighbouring atoms through the bulk of the material and re-emitted on the opposite side of the object. If the material is opaque, then the vibrations of the electrons are not passed from atom to atom through the bulk of the material, but rather the electrons vibrate for short periods of time and then re-emit the energy as a reflected light wave. The light may be re-emitted from the surface of the material at a different wavelength, thus changing its colour.

Objectives

After studying this unit, you should be able to

- understand interaction of radiation with matter
- know about difference between thermal and photochemical process
- explain different laws of photochemistry and Jablonsky diagram
- describe fluorescence, phosphorescence and non-radiative processes
- define quantum yield and photosensitized reactions

3.2 DIFFERENCE BETWEEN THERMAL AND PHOTOCHEMICAL PROCESSES

Photochemical reactions take place on the absorption of radiations (photons) by

molecules, whereas thermal reactions are initiated by the absorption of heat energy, manifested by an increase of temperature. The former reactions also include the study of reverse processes in which the energy of the chemical reaction is emitted as radiation. Thermal reactions differ from photochemical reactions in number of ways.

1. Thermal reactions take place mainly in the rotationally-vibrationally excited states while remaining in the ground electronic state. The energy is distributed between molecules according to the Maxwell-Boltzmann's distribution law (In the molecular beam reactions the reactions can be mono-energetic, but such studies are very recent and involve sophisticated methods). In photochemical reaction energy can be located in any one particular quantum state and hence a particular bond can be broken in a molecule if it absorbs mono-chromatic radiation of an appropriate frequency. The energy of absorption is given by the well known Bohr's relation: $\Delta E = h \nu$.
2. Pyrolysis of complex molecules leads to large number of free radicals and molecular fragments with Maxwell-Boltzmann's distribution of energies. These free radicals at high temperatures are highly reactive and short lived and hence have a very low concentration. Photochemically, with selection of a proper wavelength, a selective bond rupture can be achieved even at low temperature with large concentrations.
3. The photochemical reactions can be distinguished from thermal reactions, firstly by relatively large concentrations of highly excited species, which may react faster than the ground state species and may even participate isothermally in the processes that are endothermic for the latter and secondly, the electronic excitation may lead to the new electronic configuration of the molecule (for example cis-trans isomerization).
4. Thermal activation takes place by collision between the reactive species with itself or with other reactants or even with vessel containing the reaction mixture. There is no way of controlling the energies of the colliding molecules and thermal energy may be distributed among all the modes of excitation in the species. In a molecule these modes include translational, rotational and vibrational excitations. The electronic excitation mode can be excited but its population at room temperature will be negligibly small and can be confirmed from the Boltzmann's distribution, i. e. if n1 and n2 are the population of the molecules in the ground and first excited singlet state populated by the 500 nm photon (corresponds to energy commonly used in chemical reactions) the population ratio in these two non-degenerate states is given by the equation

$$n_2 / n_1 = \exp(-\Delta E/RT)$$

where $\Delta E = N_{av} h \nu = N_{av} h c/\lambda$, where N_{av} is Avogadro's number, h is Planck's constant and ν (or λ) is frequency (or wavelength) of the photon.

$$\Delta E = (6.02\text{x}10^{23})\ (6.626\text{x}10^{-34}\ \text{J s})\ (3\text{x}10^{8}\ \text{ms}^{-1})/\ 500\times10^{-9}\ \text{m})$$

$$= 238.3\ \text{kJ mol}^{-1}$$

$$n_2 / n_1 = \exp(-238.3\text{x}1000/8.314\text{x}298) = 2.66 \times 10^{-42}$$

The same calculations suggest that to have 1% population in the above excited state one needs 6260 K. Normal experience suggests that all the molecules would undergo rapid decomposition at this temperature in the ground state. Whereas in a photochemical reaction molecules can be excited electronically, using 500 nm radiation at room temperature. The concentration of the molecules produced in the excited state depends up on a number of factors, e. g. intensity of the radiation source and rate of decrease of excited molecules by many competing processes (discussed later). Further a particular species can be excited in the presence of large number of other molecules which do not absorb radiation in the same region. If this energy is used in the bond rupture of the molecule, the chemical reactions can take place.

3.3 LAWS OF PHOTOCHEMISTRY

Some of the important laws of photochemistry are:

3.3.1 Grotthuss – Draper law

The Grotthuss–Draper law (also called the Principle of Photochemical Activation) states that only that light which is absorbed by a system can bring about a photochemical change. Materials such as dyes and phosphors must be able to absorb "light" at optical frequencies. This law provides a basis for fluorescence and phosphorescence. The law was first proposed in 1817 by Theodor Grotthuss and in 1842, independently, by John William Draper.

This is considered to be one of the two basic laws of photochemistry. The second law is the Stark–Einstein law, which says that primary chemical or physical reactions occur with each photon absorbed.

3.3.2 Stark – Einstein law

The Stark–Einstein law is named after German-born physicists Johannes Stark and Albert Einstein, who independently formulated the law between 1908 and 1913. It is also known as the photochemical equivalence law or photoequivalence law. In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction.

The photon is a quantum of radiation or one unit of radiation. Therefore, this is a single unit of EM radiation that is equal to Planck's constant (h) times the frequency of light. This quantity is symbolized by γ, $h\nu$, or $\hbar\omega$.

The photochemical equivalence law is also restated as follows: for every mole of a substance that reacts, an equivalent mole of quanta of light are absorbed. The formula is:

$$\Delta E_{mol} = N_A h\nu = N_A hc / \lambda$$

where N_A is Avogadro's number.

The photochemical equivalence law applies to the part of a light-induced reaction that is referred to as the primary process (i.e. absorption or fluorescence).

In most photochemical reactions the primary process is usually followed by so-called secondary photochemical processes that are normal interactions between reactants not requiring absorption of light. As a result such reactions do not appear to obey the one quantum–one molecule reactant relationship.

The law is further restricted to conventional photochemical processes using light sources with moderate intensities; high-intensity light sources such as those used in flash photolysis and in laser experiments are known to cause so-called biphotonic processes; i.e., the absorption by a molecule of a substance of two photons of light.

3.4 JABLONSKI DIAGRAM DEPICTING VARIOUS PROCESSES OCCURRING IN THE EXCITED STATE

The Jablonski diagram (Figure 1) offers a convenient representation of the excited state structure and the relevant transitions. Molecules that have become electronically excited subsequent to the absorption of visible (400~700nm), UV (200~400nm), or NIR (700~1100 nm) radiation. Excitation process from the ground state to the excited state is very fast, on the order of 10–15 s. After excitation, the molecule is quickly relaxed to the lowest vibrational level of the excited electronic state. This rapid vibrational relaxation process occurs on the time scale of femto seconds to picoseconds. Fluorescence emission occurs as the fluorophore decay from the singlet electronic excited states to an allowable vibrational level in the electronic ground state. The fluorescence excitation and emission spectra reflect the vibrational level structures in the ground and the excited electronic states, respectively.

The diagram shows the excitation of an electron from the electronic-vibrational ground state S_0 to excited states S_1, S_2 which are characterized by the different electronic energies and by different vibrational states of the molecule. In other words: The absorption of a photon of suitable energy usually takes place between the state of lowest vibrational energy of an electronic ground state to an excited electronic state according to the Franck-Condon principle.

The absorption to a triplet state is forbidden as a consequence of quantum theory, because it would require a reversal of the electron spin. The probability of such a reversal is very low and corresponding absorption bands are therefore very weak.

The excited electron can revert to the ground state in several ways:

Deactivation processes

Internal conversion refers to the dissipation of vibrational energy to different vibrational modes in the molecule or to the dissipation of vibrational energy to vibrational or translational energy of other molecules, for example in interactions (collisions) with the solvent in which the excited molecule is diluted. This is an exchange by which the molecule returns to thermodynamical equilibrium with its environment. The molecule reverts to the vibrational ground state of the corresponding electronically excited state.

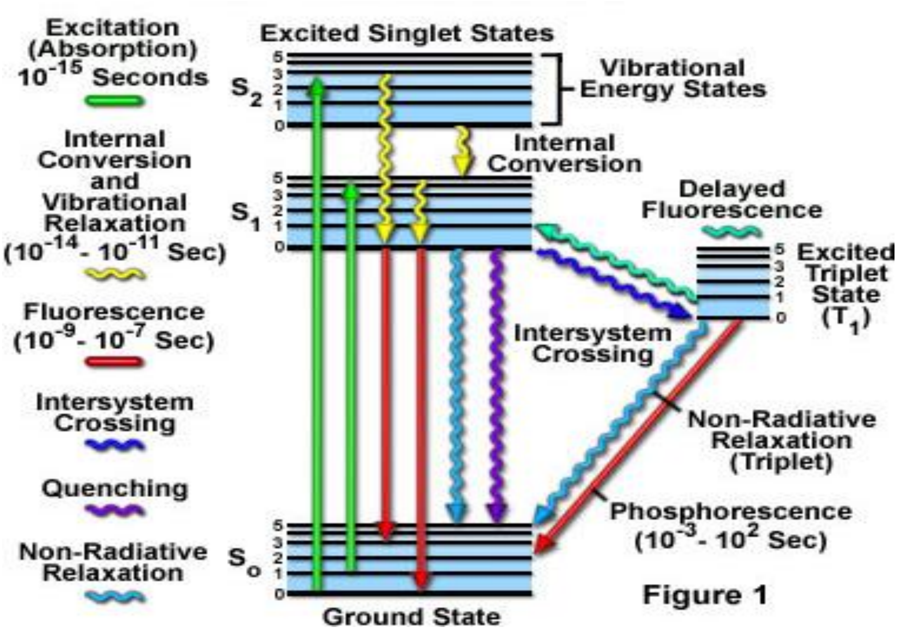


Figure 1 JABLONSKI DIAGRAM

Nonradiative deactivation

By this mechanism the electronic energy is converted into vibrational energy which is then dissipated to the environment. Similarly to vibrational relaxation, all electronic energy is dissipated in form of vibrational and translational energy to the environment of the molecule. The same process is also responsible for the relaxation of electronic states like S_2 or higher to the S_1 state (an exception is azulene, which shows fluorescence from the S_2 state). One could imagine that nonradiative deactivation also leads to the relaxation of the S_1 state to the electronic ground state S_0. However, the energy difference between the electronic ground state and the S_1 state is higher than the energy difference between S_1 and electronic states of even higher energy. The nonradiative transition between the excited S_1 state and the ground state S_0 therefore requires the concurrent excitation of many vibrational modes which is more unlikely to take place. Therefore, the nonradiative transition from the S_1 to the S_0 state is much slower and Fluorescence can successfully compete with the nonradiative process.

Intersystem crossing

Intersystem crossing is a spin-exchange mechanism by which singlet states can be converted into triplet states and triplet states can be converted into singlet states. This transition is only rarely observed.

In **fluorescence quenching** the excitation energy is transferred to special quencher molecules.

Fluorescence is the observed radiation when an electron makes the transition from the lowest vibrational mode of the electronically excited state S_1 to a vibrational mode of the electronic ground state S_0. The rate of such a transition is in the region of 10^7 to 10^8 s^{-1}.

Phosphorescence is the observed radiation when the electron makes the transition from the lowest vibrational mode of a triplet state, T_1, into a vibrational mode of the singlet state S_0.

The rate of this transition can be 10^4 s^{-1} to value < 1 s^{-1}. The different possible transitions are depicted in Figure. The Fluorescence that shall be discussed in this chapter has the following properties:

A. the spectrum of the emitted radiation is independent of the wavelength of excitation.
B. the spectrum is shifted towards longer wavelength (corresponding to smaller frequencies and therefore to smaller energy ($c=\nu.\lambda$ and $E=h\nu$).
C. while the fine structure of the absorption spectrum is characterized by the vibrational modes of the excited state (S_1), the fine structure of the fluorescence spectrum is characterized by the vibrational modes of the electronic ground state (S_0). If the vibrational modes of the ground state S_0 and the excited S_1 state are comparable, the absorption an the fluorescence spectra relate to each other like an image to its mirror.

3.5 QUALITATIVE DESCRIPTION OF FLUORESCENCE

Fluorescence, a type of luminescence, occurs in gas, liquid or solid chemical systems. Fluorescence is brought about by absorption of photons in the singlet ground state promoted to a singlet excited state. The spin of the electron is still paired with the ground state electron, unlike phosphorescence. As the excited molecule returns to ground state, it involves the emission of a photon of lower energy, which corresponds to a longer wavelength, than the absorbed photon.
The energy loss is due to vibrational relaxation while in the excited state. Fluorescent bands center at wavelengths longer than the resonance line. This shift toward longer wavelengths is called a Stokes shift. Excited states are short-lived with a lifetime at about 10^{-8} seconds. Molecular structure and chemical environment affect whether or not a substance luminesces. When luminescence does occur, molecular structure and chemical environment determine the intensity of emission. Generally molecules that fluoresce are conjugated systems. Fluorescence occurs when an atom or molecules relaxes through vibrational relaxation to its ground state after being electrically excited. The specific frequencies of excitation and emission are dependent on the molecule or atom.

$$S_0 + h\nu_{ex} = S_1$$

where $h\nu$ is a photon energy with h is Planck's constant and ν is the frequency of light, S_0 is the ground state of the fluorophore and S_1 is its first electronically excited state.

The fluorescence quantum yield ((\Φ\)) gives the efficiency of the fluorescence process. It is the ratio of photons emitted to photons absorbed.

$$\Phi = \# \text{ emitted photons} / \# \text{ absorbed photons}$$

If every photon absorbed results in a photon emitted. The maximum fluorescence quantum yield is 1.0, and compounds with quantum yields of 0.10 are still considered fluorescent. Another way to define the fluorescence quantum yield is by the excited state decay rates:

$$\Phi = kf / \sum iki$$

where kf is the rate of spontaneous emission of radiation and the denominator is the sum of all rates of excited state decay for each deactivation process (ie phosphorescence, intersystem crossing, internal conversion…). The fluorescence lifetime is the average time the molecule remains in its excited state before emitting a photon. Fluorescence typically follows first-order kinetics:

$$[S_1] = [S_1]_o e^{-t/\tau}$$

Where $[S_1]$ is the concentration of excited state molecules at time t, $[S_1]_0$ is the initial concentration and τ is the decay rate.

Various radiative and non-radiative processes can de-populate the excited state so the total decay rate is the sum over all rates:

$$\tau_{tot} = \tau r_{ad} + \tau nr_{ad}$$

where τ_{tot} is the total decay rate, τr_{ad} the radiative decay rate and τnr_{ad} the non-radiative decay rate. If the rate of spontaneous emission or any of the other rates are fast, the lifetime is short. The average lifetime of fluorescent compounds that emit photons with energies from the UV to near infrared are within the range of 0.5 to 20 nanoseconds.
The fluorescence intensity, IF is proportional to the amount of light absorbed and the fluorescence quantum yield, Φ

$$I_f = kI_o\phi\ [1-(10^{-\varepsilon bc})]$$

Where k is a proportionality constant attributed to the instrument, \(I_o\(is incident light intensity, ϵ is the molar absorptivity, b is the path length, and c is the concentration of the substrate.
If dilute solutions are used so that less than 2% of the excitation energy is absorbed, then an approximation can be made so that

$$10x \approx 1 + x + \ldots$$

so the above equation can be simplified to

$$If = kIo\Phi[\varepsilon bc]$$

This relationship shows that fluorescence intensity is proportional to concentration.
Fluorescence rarely results from absorption of UV-radiation of wavelengths shorter than 250 nm because this type of radiation is sufficiently energetic to cause deactivation of the excited state by predissociation or dissociation. Most organic molecules have at least some bonds that can be ruptured by energies of this strength. Consequently, fluorescence due to $\sigma* \rightarrow \sigma$ transitions is rarely observed. Instead such emission is confined to the less energetic $\pi* \rightarrow \pi$ and $\pi* \rightarrow n$ processes. Fluorescence commonly occurs from a transition from the lowest vibrational level of the first excited electronic state to the one of the vibrational levels of the electronic ground state. Quantum yield (Φ) is greater for $\pi* \rightarrow \pi$ transition because these excited states show short average lifetimes (larger *kf*) and because deactivation processes that compete with fluorescence is not as likely to happen. Molar absorptivity of $\pi \rightarrow \pi^*$ transitions is 100-1000 fold greater. The average lifetime is 10^{-7} to 10^{-9}seconds for π, π * states and 10^{-5} to 10^{-7} seconds for n, π* states.

3.6 PHOSPHORESCENCE

Unlike florescence, phosphorescence does not re-emit the light immediately. Instead, phosphorescence releases light very slowly in the dark due to its energy transition state. When light such as ultraviolet light is shined upon a glow in dark object, the object emits light, creating phosphorescence.

There is a similarity between the phosphorescent and the fluorescent materials. They both contain substances with identical atoms. It is very important to understand the impurity state energy band, which is located between the conduction and valence energy bands. In a phosphorescence event, the absorbed energy usually goes through a high energy state which happens to be triplet state. The energy gets trapped in the triplet state because its physical situation forbids the transition to return to lower energy state, also as known from impurity to valence band. In order to change the energy of valence band, electrons must regain the energy they had lost during the impurity band transitional process. If the quantum yield of the phosphorescence is high enough, a great amount of light will be released and thus making the object glow in the dark.

Most compounds have the ground state of singlet S_0. When it absorbs light, the electrons in the molecule may move to excited state of S_1, S_2, S_n and so on. There are also triplet states T_1 and T_2. The energy of the T_1 state is typically below the S_1 state, while T_2 is between S_2 and S_1 state. The wavelength of the radiation can determine which state the electron will move to. It is possible for the electron to return from excited state back to the ground state. An example is phosphorescence, where the emitting of radiation demotes the electrons from the excited state of T_1 to ground state S_0. The molecule of phosphorescence has long life time, it loses energy easily, so it is hard to observe phosphorescence.

Materials that can produce phosphorescence often contain zinc sulfide, sodium fluorescein, rhodamine, or strontium. The majority of phosphorescence is often used in drugs in pharmaceutical field. Some common drugs that have phosphorescence property include Aspirin, benzoic acid, morphine, and dopamine. Phosphorescence is also used to analyze water, air and chemical pollutions.

3.7 NON-RADIATIVE PROCESSES (INTERNAL CONVERSION, INTERSYSTEM CROSSING)

The return of the molecule from excited state to ground state may also occur by non-radiative processes. Two of these processes are important: (a) Internal conversion and (b) Intersystem crossing

Internal conversion is a transition from a higher to a lower electronic state in a molecule or atom. It is sometimes called "radiationless de-excitation", because no photons are emitted. It differs from intersystem crossing in that, while both are radiationless methods of de-excitation, the molecular spin state for internal conversion remains the same, whereas it changes for intersystem crossing. The energy of the electronically excited state is given off to vibrational modes of the molecule. The excitation energy is transformed into heat.

Examples

A classic example of this process is the quinine sulfate fluorescence, which can be quenched by the use of various halide salts. The excited molecule can de-excite by increasing the thermal energy of the surrounding solvated ions.

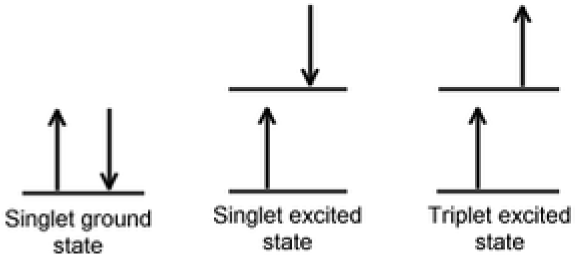
Several natural molecules perform a fast internal conversion. This ability to transform the excitation energy of photon into heat can be a crucial property for photoprotection by molecules such as melanin. Fast internal conversion reduces the excited state lifetime and thereby prevents bimolecular reactions. Bimolecular electron transfer always produces a reactive chemical species, free radicals. Nucleic acids (precisely the single, free nucleotides, not those bound in a DNA/RNA strand) have an extremely short lifetime due to a fast internal conversion.

Both melanin and DNA have internal conversion rates that are many orders of magnitude faster than any man-made molecule.

Intersystem crossing is a radiationless process involving a transition between two electronic states with different spin multiplicity. Excited electrons can undergo intersystem crossing to a degenerate state with a different spin multiplicity.

Singlet and triplet states

When an electron in a molecule with a singlet ground state is excited (*via* absorption of radiation) to a higher energy level, either an excited singlet state or an excited triplet state will form. A singlet state is a molecular electronic state such that all electron spins are paired. That is, the spin of the excited electron is still paired with the ground state electron (a pair of electrons in the same energy level must have opposite spins, per the Pauli exclusion principle). In a triplet state the excited electron is no longer paired with the ground state electron; that is, they are parallel (same spin). Since excitation to a triplet state involves an additional "forbidden" spin transition, it is less probable that a triplet state will form when the molecule absorbs radiation.



Singlet and triplet energy levels

When a singlet state nonradiatively passes to a triplet state, or conversely a triplet transitions to a singlet, that process is known as intersystem crossing. In essence, the spin of the excited electron is reversed. The probability of this process occurring is more favorable when the vibrational levels of the two excited states overlap, since little or no energy must be gained or lost in the transition. As the spin/orbital interactions in such molecules are substantial and a change in spin is thus more favourable, intersystem crossing is most common in heavy-atom molecules (e.g. those containing iodine or bromine). This process is called "spin-orbit coupling". Simply-stated, it involves coupling of the electron spin with the orbital angular momentum of non-circular orbits. In addition, the presence of paramagnetic species in solution enhances intersystem crossing.

The radiative decay from an excited triplet state back to a singlet state is known as phosphorescence. Since a transition in spin multiplicity is observed, phosphorescence is another manifestation of intersystem crossing. The time scale of intersystem crossing is on the order of 10^{-8} to 10^{-3} s, one of the slowest forms of relaxation.

3.8 QUANTUM YIELD

Quantum yield is the major characteristics of a photochemical reaction. The quantum yield, also called the quantum efficiency, is defined as the number of events occurring per photon absorbed. These events might be related to physical processes responsible for energy dissipation (such processes are discussed in Basic Photophysics), but they also might be related to molecules of a chemical product formed upon photoirradiation. Generally, the (total) quantum yield of a photoreaction, ϕ, is:

(1)

$$\phi = \frac{\text{number of molecules undergoing the reaction of interest}}{\text{number of photons absorbed by the photoreactive substance}}$$

Eq. (1) would define the quantum yield of product formation, ϕ_p, if the number of product molecules would be determined. If the two numbers in Eq.(1) are measured per time and volume unit then the quantum yield is expressed in terms of rates

(2)

$$\phi = \frac{\text{rate of the reaction of interest}}{\text{rate of light absorption by the photoreactive substance}}$$

The latter quantity is also referred to as the differential quantum yield. Notice that these two definitions of the quantum yield agree only if the yield is constant during the course of the reaction. Eqs.(1) and (2) indicate that two separate measurements may be required to determine a quantum yield. In the simplest set-up, a reaction cell is mounted in a fixed position relative to the light source. The cell is charged with the sample of interest and irradiated. Photochemical conversion is determined with a suitable experimental technique (spectroscopy, chemical analysis, etc.). Afterwards, the cell is replaced with an actinometer, which is also irradiated.

For primary processes, the quantum yield ranges from 0 to 1—an efficiency of 0% to 100%. For secondary processes, the quantum yield can be greater than 1. For chain reactions, which produce many product molecules for every photon absorbed, the quantum yields can be as high as one million. The quantum yields observed in practise may vary from 0 to 10^6.

3.9 PHOTOSENSITIZED REACTIONS- ENERGY TRANSFER PROCESSES (SIMPLE EXAMPLES)

In photochemistry, photosensitized reactions have attracted the chemists from different areas of chemistry as the route is simple as well as low-cost in comparison to the other photochemical techniques. Due to this fact, the field of the photosensitized reactions is now growing field today for all chemists. Its application is not limited to any specific branch of chemistry but the technique can be applied in different area of chemistry. The most important feature of these reactions is the very less amount of the photosensitizer is required for the completion of the reaction. This can also help us to protect our environment against the chemical pollution; which is again fulfilling the condition of one of the twelve green chemistry principles.

Certain reactions, though not sensitive to light, are made sensitive by the presence of small quantity of substance. The foreign substance can absorb light and stimulate the reaction without taking part in it. The substance which after absorbing light induces a photochemical reaction without undergoing any chemical reaction is known as sensitizer and this phenomenon is known as photosensitization. Photosensitized reactions are the reactions in which; the light-absorbing molecule transfers its energy to another molecule and itself comes to the ground state. The energy-accepting molecule goes to excited state and gives chemical reaction.

Different compounds are used as photosensitizer such as ketones, aliphatic and aromatic amines, methylene blue, eosin, eosin yellow, rose bengal, acridin orange, chlorophyll, hematoporphyrin, carbazole, naphthalene and its derivatives, anthracene, riboflavin, dienes, hydroquinones, borohydride, mercury, ozone, H_2O_2, UV/H_2O_2, UV/O_3, UV/Fenton’s reagent, organometallic complexes and many more compounds are reported as photosensitizer in different applications. A wide range of chemicals, including some that are fungal and bacterial in origin, may act as photosensitizing agents.

3.9.1 Mechanism of photosensitized reaction

This type of reaction is known as indirect photochemical reaction in which the photons of visible light are not directly absorbed by the substrate molecule but the energy for performing photochemical reaction is received from the sensitizer. As these reactions can be performed with the help of visible light which is available freely, cost of the reaction can be reduced. In this reaction, the photosensitizer molecule (Donor) will first absorb the visible light frequency and it will get into the singlet excited state. By inter system crossing (ISC), it will get into the triplet excited state; where the life time of the excited species is very less and by transferring the energy from triplet state to the substrate molecule (Acceptor), the photosensitizer will come back to the ground state. By this energy transfer process, substrate molecule will get into the singlet excited state and from there and ultimately result in chemical alteration of the other molecule in the system (Fig. 2)

$$D \xrightarrow{h\nu} D^{*1}$$

$$D^{*1} \xrightarrow{ISC} D^{*3}$$

$$D^{*3} + A \longrightarrow A^{*1} + D$$

$$A^{*1} \longrightarrow \text{Product}$$

Figure 2: General mechanism of photosensitized reaction

3.9.2 Types of Photosensitized reaction

Mainly there are two types of photosensitized reactions. First type is by electron transfer and second is by energy transfer. Generally these types of reactions are oxidation reactions which are also known as photooxidation reactions. For type one, there is either hydrogen atom abstraction or electron transfer and radical will be formed and then radical will react with oxygen to give oxidation product while for type two, energy transfer occurs between excited sensitizer and oxygen giving excited singlet oxygen from which; the oxidation product will be formed. Singlet oxygen has special physical properties; which allow characterization of it and the photosensitized mechanism can be derived for a particular reaction.

3.9.3 Application of photosensitized reaction

Due to the practicality and versatility of the reaction, photosensitized reactions are in high demand in the chemical research field. Today almost in each and every field photochemical reactions are being studied. Furthermore, the cost effectiveness of the reaction adds more value in today's research. These reactions which involve UV/Vis radiation and biological systems are particularly interesting because of their wide field of applications such as environmental, energetic, biological, medical, polymer etc. In pharmaceutical field, photosensitized reactions are used for the discovery and synthesis of new drug molecules at bigger scale which; definitely leads the industries towards the green chemistry and eco-friendly approach.

Even some of the drug molecules shows the photosensitizer's properties and reactions are being carried out using drug molecules too in pharmaceutical industries. In polymer industries, number of photosensitized reactions are performed to get new polymers which reduces the cost of production. Today the whole world is struggling against the problem created due to the pollution of soil, water and air and photochemical reactions have demonstrated high level of satisfaction for the treatment of polluted soil, water and air samples. Thus in water treatment process, photosensitized reactions are proven as one of the best and economic techniques. In biology, photosensitized reactions are popular in aerobic and anaerobic conditions in the presence of different bacteria. In medical field, nowadays therapeutic approach for the treatment of some of the incurable cancer cells is possible due to the photosensitized reactions. In other medical fields like photodynamic therapy, blood purification and in the process of inactivation of viruses, photosensitized reactions are proved very useful. Today, in the development of industries like polymer, agrochemical, pesticides, rubber, fine chemicals, solvents, dyes and intermediates, textile, etc., the applications of photosensitized reaction have played an important and dynamic role. Different photosensitizers work differently and it is not possible to give the mechanism of all those sensitizers here. But in general they follow the same basic mechanism as discussed above.

3.10 SUMMARY

In this unit you have studied about the brief introduction of the photochemistry about fundamental principles of photochemistry, the process and laws of photochemistry, brief explanation on Jablonsky diagram depicting various processes and defining the process of the photosensitizations.

3.11 TERMINAL QUESTIONS

1. Draw and label the Jablonski Diagram.
2. What is quantum yield and how is it used to compare the fluorescence of different types of molecule?
3. Calculate the energy associated with (a) one photon or quantum (b) one Einstein of radiation of wavelength 530 nm. [Hint: Energy of a photon =hc/λ, Energy per Einstein = N [hc/λ]
4. A system absorbs 2.0×10^{16} quantum of light per second. At the end of 20 min and 4s.it is observed that 0.02 moles of the irradiated substances had reacted. Calculate the quantum efficiency.
5. The Vividh Bharti station of All India Radio, Delhi broadcasts on a frequency of 1368 kHz. Calculate the wavelength of the electromagnetic radiation emitted by transmitter.
6. What is meant by photosensitisation.
7. Define fluorescence and phosphorescence.
8. When gaseous HI is illuminated with a radiation of wavelength 2530 Å, it is observed that 1.85×10^{-2} mole decomposes per 1000 cal of radiant energy absorbed. Calculate quantum yield.
9. The wavelength of beam of light is 2.80×10^{-5} m. Calculate its: (a) wavelength in cm, (b) frequency and (c) the energy of a photon.
10. Calculate the magnitude of energy associated with a photon (or quantum) of light wavelength 600 nm.

3.12 ANSWERS

3. 3.76×10^{-19} J, 2.26×10^{5} J

4. 50.02

5. 219.3 m

8. 2.09

9. (a) 2.80×10^{-4} cm, (b) 1.07×10^{13} Hz, (c) 7.06×10^{-21} J.

10. 3.315×10^{-19} J

UNIT 4: VIBRATIONAL, ROTATIONAL AND ELECTRONIC SPECTROSCOPY

Structure

4.1. Introduction

'Spectro' means radiation and 'scopy' means measurement. Thus spectroscopy means measurement of radiations. This is a branch of science which is associated with interaction of radiations of different wavelengths with matter. Currently Spectroscopy is proved to be the most rigorous method of analysis of organic and inorganic compounds.

When a sample is exposed to radiation of certain range there occurs rotational, vibrational or electronic transitions. Each of these transitions may be correlated to the frequency of radiation is absorbed on this basis there are different types of spectroscopic techniques. Each of these techniques has a particular application. Microwave spectra may be used for the determination of bond distance. IR spectra lead to the determination of force constant. From electronic spectra, inorganic and organic groups may be identified.

Objective:

After studying this unit, you should be able to:

- Know about different types of spectroscopic techniques.
- Derive mathematically the expressions for energy levels of rotational and vibrational spectra.
- Change in the value of rotational constant, due to isotope effect.
- Calculate bond length of CO, NO, HCl etc. when rotational spectrum is given.
- Calculate the value of force constant for different molecules.
- Explain intensity of electronic spectrum.
- Understand different types of molecular orbitals present in the molecules.
- Explain which electronic transition requires higher frequency and which one lower frequency.
- Explain the types of molecules which are IR active or Raman active or microwave active.
- Explain the vibrational or rotational transitions on the basis of selection rules of various spectra.

Rotational Spectrum

4.2 Brief idea about rotational or microwave spectroscopy

The microwave rotational Spectroscopy explores that part of the electromagnetic spectrum which is extending from 100 nm ($3x10^{13}$ Hz) to 1 cm ($3x10^{10}$ Hz). This region is called the microwave region. This lies between far infrared and radio frequency region. Its Applications are based on absorption rather than emission. Microwave Spectroscopy has been found to be very useful in the determination of the structures of those molecules which do not give good results by using Raman and infrared spectroscopy. Perhaps, Microwave, IR and Raman all are completely different techniques it is very unfair to say which one much better because all of them gather different kinds of knowledge of molecules. The ability to measure frequencies in the microwave region allows very accurate calculations of the order of 0.001 angstrom then in the infrared-visible-ultraviolet.

Microwave Spectroscopy deals with pure rotational motion of molecules. The condition that is essential for observing resonance in this region is that a molecule must possess permanent dipole moment e.g. CO, NO, HCl, H_2O vapour etc. When a molecule having dipole moment it rotates, it generates electric field which can interact with the electric component of the microwave radiation. During the interaction, energy can be absorbed or emitted and thus the rotation of the molecule gives rise to a spectrum. Hetero diatomic and polyatomic molecules with permanent dipole moment give rise to a spectrum which are said to be microwave active. However polyatomic molecules having no dipole moment may be made to undergo radical rotational transition because of the fact that exciting radiation can induce an oscillating dipole moment in such type of molecules. If molecules are not having dipole moments, (e.g homonuclear molecules such as N_2, O_2, H_2, Cl), interaction is not possible and these molecules are said to be microwave inactive.

Diatomic molecules

4.3. Energy levels of rigid Rotor (Semi Classic Principles)

On the basis of wave mechanics, it can be seen that if a diatomic molecule is considered to be a rigid rotator, i.e, like a rigid dumbbell joined along its line of centre's by a bond equal in length to the distance. Between the two nuclei, then the allowed rotation energies how the molecule around access passing through the centre of gravity and perpendicular to the line joining the nuclei are given by:

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \text{...............}(1)$$

Where J is rotational quantum number that can have values 0,1,2,3 etc. and I is the moment of inertia of the molecule about the axis of rotation, i.e

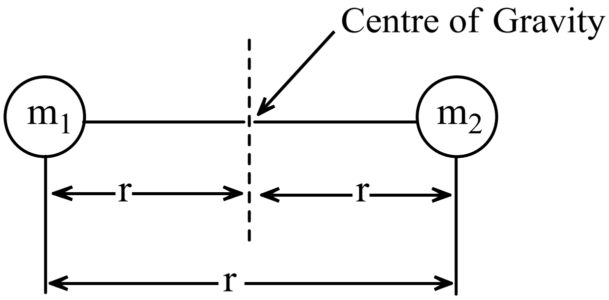


Fig.1 Rigid Rotors

$$I=\left(\frac{m_1 m_2}{m_1+m_2}\right) r_o^2=\mu r_o^2 \qquad \text{................}(2)$$

Where m_1 and m_2 are the atomic masses of the two atoms of the diatomic molecule and

$$\left(\frac{m_1 m_2}{m_1+m_2}\right)=\mu \qquad \text{................}(3)$$

Derivation of the expression for the rotational energy: Centre of gravity of a diatomic molecule is the point which satisfies the following conditions-

$$m_1 r_1 = m_2 r_2 \qquad \ldots\ldots\ldots\ldots.(4)$$

$$I = m_1 r_1^{\,2} + m_2 r_2^{\,2} \qquad \text{.............}(5)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 \,(m_2 + m_1) \qquad \text{.............}(6)$$

$$(\text{But, } r_1 + r_2 = r_o) \qquad \text{.............}(7)$$

Substituting these values in eq. (5), we get-

$\therefore$ From equation (4) $\quad m_1r_1 + m_2(r_0\text{-}r_1)$

$$\text{Or, } r_1 = \frac{m_1r_0}{m_1 + m_2} \quad \text{............(8)}$$

$$\text{Similarly, } r_2 = \frac{m_1r_0}{m_1 + m_2} \quad \text{............(9)}$$

Substituting these values in eq. (5), we get-

$$I = \frac{m_1m_2^2}{(m_1 + m_2)^2}\, r_0^2 + \frac{m_1^2m_2}{(m_1 + m_2)^2}\, r_0^2$$

$$= \frac{m_1m_2(m_1 + m_2)}{(m_1 + m_2)^2}\, r_0^2 = \frac{m_1m_2}{m_1 + m_2}\, r_0^2$$

$$= \mu r_0^2 \text{ (where } \mu = \frac{m_1m_2}{m_1 + m_2} \text{ is reduced mass)} \quad \text{.............(10)}$$

Now, by definition, the angular momentum of a rotating molecule is given by:

$$L = I\omega \quad \text{................(11)}$$

Where ω is the angular velocity (just as linear momentum is mass x velocity). But we know that angular momentum is quantized whose values are given by-

$$L = \sqrt{J(J+1)}\,\frac{h}{2\pi} \quad \text{................(12)}$$

Where J=0, 1, 2, 3,...... called the rotational quantum numbers. Further the energy of a rotating molecule is given by -

$$E = I\omega^2 \quad \text{................(11)}$$

The quantized value of the rotating molecule is given by-

$$E_r = \frac{h}{2\pi}\, I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad \text{................(12)}$$

Substituting the value of L from equation (12), we get-

$$E_r = J(J+1)\frac{h^2}{4\pi^2} \times \frac{1}{2I}$$

Or,

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \text{.............(14)}$$

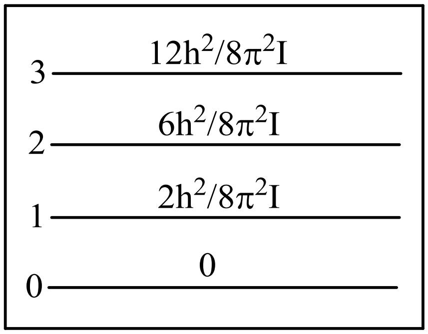


Fig.2 Rotational energy levels of a diatomic molecule treating it as a rigid rotor.

Putting J=0, 1, 2, 3, etc equation (1), pattern of the rotational energy levels obtained will be as shown in fig 2.

Evidently, the spacing between the energy levels increases as J increases.

4.4. Selection rules:

Quantum mechanical restrictions i.e., selection rule for rotational spectra:-

For a molecule to show rotational spectra, it must have a dipole moment, but all the transactions involving arbitrarily any two rotational levels are not permissible. The quantum mechanics permit only those rotational transitions in which there is an increase or decrease of unity in the rotational quantum number (J). This is the transaction in rotational energy levels is limited to only adjacent rotational levels.

Mathematically,

$$J'' - J' = \Delta J = \pm 1$$

This is called selection rule for a rotational transition for a diatomic rigid molecule. Thus, according to this rule, the rotational transitions J=0→2, J=1→ 3. J=2→0 etc. are not possible, because in such cases

$$\Delta J \neq (\pm 1).$$

Rotational spectrum consists of equidistant spectral lines:

The rotational spectra are known only in absorption. We know that,

$$\overline{V}_{rot} = B[J''(J'+1) - J'(J'+1)] \qquad \text{.......... (1)}$$

Hence variety of rotational transitions with $\Delta J \neq (\pm 1)$ would be possible, if appropriate energies are made available to the system. Thus

When J'=0 and J"=1, then

$$\overline{V}_{rot} = B[1(1+1) - 0(0+1)] = 2B\ cm^{-1}$$

When J'=0 and J"=2 then

$$\overline{V}_{rot} = B[2(2+1) - 1(1+1)] = 4B\ cm^{-1}$$

When J'=2 and J"=3, then

$$\overline{V}_{rot} = B[3(3+1) - 2(2+1)] = 6B\ cm^{-1}$$

When J'=3 and J"=4, then

$$\overline{V}_{rot} = B[4(4+1) - 3(3+1)] = 8B\ cm^{-1}$$

Thus, we see that rotational spectrum consists of a series of spectral lines with frequency separation (expressed in terms of wave number V_{rot}) of 2B cm^{-1} between the two consecutive lines. Thus, on frequency scale, the rotational spectral lines are equidistant. The frequency scale can be constructed with the help of the following general equation:

$$\overline{V}_{rot} = 2(J+1)\ B\ cm^{-1} \qquad \text{..........(2)}$$

$$[J \rightarrow (J+1)]$$

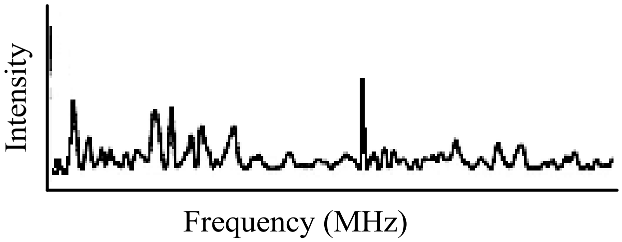
Where J=0, 1, 2, 3, 4..... respectively.

$$\text{Or,} \qquad \Delta\overline{v} - 2B \qquad \text{............(3)}$$

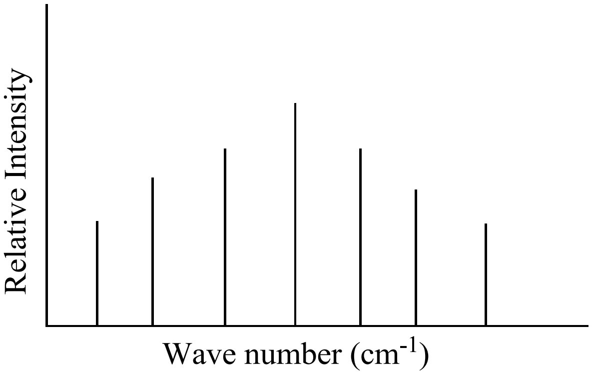
4.5 Spectral Intensity

Pure rotational spectra usually occur in the microwave region of the electromagnetic radiation. In microwave region it is frequently expressed in units of frequency (megahertz MHz or gigahertz GHz). Since rotations usually occur along with vibrations, so it is also expressed in a common unit vibrational transition, the wave number ν (cm^{-1}). Such representations are shown in Fig 1.

The intensity pattern of rotational spectra as shown in Fig.1 (b) is due to the number of molecules having a certain rotational state. This is called the population of the state. The population of each rotational state is different and hence, the number of molecules absorbing radiation and becoming excited to the next state is different. This population difference is responsible for the varying intensities of each rotational spectral line.



(a)



(b)

Fig.1- Pure rotational spectrum (intensity vs. frequency) and (b) rotational spectrum plotted in wave number unit. A statistical treatment of the energy levels indicates that the approximate maximum populated J quantum number J_{max} is given by:

$$J_{max} \approx \left(\frac{kT}{2B}\right)^{1/2} \qquad \ldots\ldots(1)$$

Where K is Boltzmann's constant, T is the absolute temperature of the sample and B is the rotational constants B for selected diatomic molecules are listed in Table.1:

Table 1- Rotational constant B for diatomic molecules.

Molecule	Rotational constant B
H_2	60.80
N_2	2.010
O_2	1.45
HCl	10.6
NO	1.17

4.6. Distribution using population distribution is relative intensities of rotational spectral lines:-

Relative intensities of spectral lines depend upon the relative population of the energy levels. As we see from Example 1. even at room temperature many of the diatomic molecules are present in the excited state energy levels. Since the energy level population is given by the Boltzmann distribution, the intensity of rotational lines is evidently proportional to the Boltzmann distribution of molecules in the rotational energy levels, i.e.

$$\text{Intensity } \alpha \ {N_j}/{N_o} = e^{{-E_j}/{K_t}}$$

Rotational energy levels are, however, degenerate, there degeneracy (g_J) for a diatomic molecule being given by-

$$g_J = 2J+1 \qquad \ldots\ldots\ldots\ldots(2)$$

In other words, for a given value of J, the energy level is (2J+1) fold degenerate. For J=1, g_J=1; for J=1, g_J=3; for J=2, g_J= 5; and so on.

Hence, the intensity of the rotational spectral lines is determined by the product of the degeneracy factor and the Boltzmann exponential factor. Thus,

$$\text{Intensity } \alpha \ {}^{N_j}\!/_{N_o} = (2J+1)e^{-Ej/kT} \qquad \ldots\ldots(3)$$

Since, $E_j = hcF(J)$ ..... (4)

And $F(J) = BJ(J+1)$ .... (5)

We have, $N_j/N_o = (2J+1)\ e^{-Bj(J+1)hc/kT}$ ....(6)

The quantity N_j/N_o is plotted versus J for a rigid diatomic molecule at room temperature in Fig. 1.

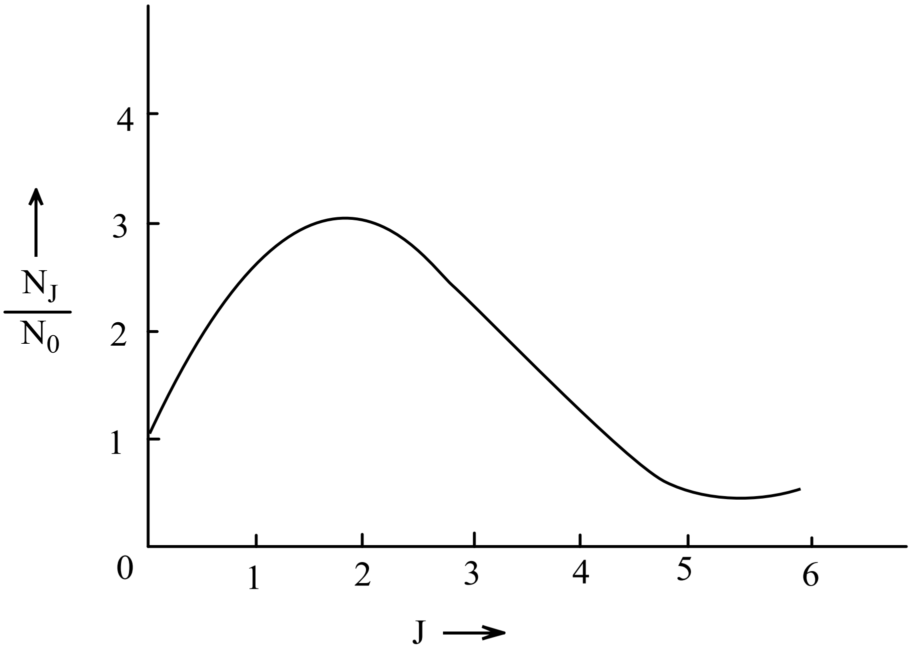


Fig.7. Plot of the relative Boltzmann population vs. J for a rigid diatomic molecule

We see that the relative intensity passes through a maximum. It can be shown that the value of J corresponding to the maximum in population is given by-

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2} \qquad \ldots\ldots(7)$$

The J Max should be rounded off to the nearest integral value.

Example 1: Calculate J_{max} for a rigid diatomic molecule for which at 300 K, the rotational constant is 1.566 cm^{-1} .

Solution-

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

$$= \left(\frac{(1.38 \text{ x } 10^{-23} \text{ JK}^{-1})(300\text{K})}{2(6.62 \text{ x } 10^{-34} \text{ JS})(3 \text{ x } 10^{10} \text{ cms}^{-1}(1.566 \text{ cm}^{-1})}\right)^{1/2} - \frac{1}{2}$$

$$= 7.56 = 8.$$

4.7 Determination of inter-nuclear distance (Bond length) from rotational spectra

Rotational spectrum is a valuable means for obtaining inter-nuclear distances. HCl shows absorption at V= 20.68 cm^{-1}. Thus, the intermolecular distance for HCl molecule may be calculated as follows:

$$\bar{\nu} = \frac{h}{4\pi^2 CI} \qquad \text{Or, } I = \frac{h}{4\pi^2 C\bar{\nu}}$$

$$\bar{\nu} = 20.68 \text{ cm}^{-1}$$

$$h = 6.62 \text{ x } 10^{-27} \text{ erg sec.} \qquad I = \text{moment of inertia}$$

$$= \mu r^2$$

$$C = 3 \text{ x } 10^{8} \text{ cm/sec.}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{Where } \mu = \text{reduced mass}$$

$$= 1.62 \text{ x } 10^{-24} \text{ g}$$

$$\text{For HCl} = \frac{\frac{1}{N} \cdot \frac{35.5}{N}}{\frac{1 + 35.5}{N}} = 1.62 \text{ x } 10^{-24} \text{ g}$$

$$\text{For HCl} = \frac{\frac{1}{N} \cdot \frac{35.5}{N}}{\frac{1 + 35.5}{N}} = 1.62 \text{ x } 10^{-24} \text{ g}$$

$$\therefore \text{ I} = 1.62 \text{ x } 10^{-24} \text{ g.r}^2 \qquad \text{..........(1)}$$

$$\text{Also I} = \frac{6.62 \text{ x } 10^{-27}}{4 \text{ x } (3.14)^2 \text{ x } 3 \text{ x } 10^{10}\ 20.68}$$

$$\text{I} = 2.71 \text{ x } 10^{-40} \text{ g.cm}^2 \qquad \text{........(2)}$$

Now on substitution of value of I from (2) in equation (1),

$$2.71 \text{ x } 10^{-40} = 1.62 \text{ x } 10^{-24}\, \text{r}^2$$

$$\text{Or, r} = \sqrt{\frac{6.62 \text{ x } 10^{-27}}{1.62 \text{ x } 10^{-24}}}$$

$$= 1.30 \text{ x } 10\text{-}8 \text{ cm} \quad \text{or } 1.30 \text{ Å}$$

4.8 Qualitative description of non rigid rotor

It is quite obvious that the molecule cannot be strictly rigid rotator, when it is also able to perform vibrations. Therefore, a better model for representing the rotation of the molecule is to consider the diatomic molecule as a rotating system consisting of two atoms connected by a massless spring. This simple picture of a diatomic molecule is commonly known as non rigid rotator model. The energy of rotation is then expressed as-

$$E_y = \frac{h}{4\pi^2 C\bar{\nu}} [J(J+1)] - Dh[J^2(J+1)^2] \text{ ergs}$$

In which D is a centrifugal distortion constant and it is of order of 10^{-4} B.

It is a small positive quantity and is given by-

$$D = \frac{4B^3}{(\bar{\nu}o)^2}$$

Where $\bar{\nu}_o$= fundamental vibrational frequency.

As $\bar{\nu}_o$ and is always very much greater than and B and therefore according to above equation D will be much smaller than B.

The selection rule [Δ J ≠ ±1] is valid whether rotator is rigid or non-rigid. The frequency (in terms of wave number $\bar{\nu}_{rot}$) of rotational spectra line, representing the transition for J to (J+1) is given by -

$$\bar{\nu}_{rot} = 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1}$$

$$[J \rightarrow (J+1)]$$

The frequency of rotational spectral lines for the transition from J to (J+1), rotational energy can be calculated using above equation.

$$\underset{J=0\rightarrow 1}{\bar{\nu}_{rot}} = 2B(0+1) - 4D(0+1)^3 = (2B - 4D) \text{ cm}^{-1}$$

$$\underset{J=1\rightarrow 2}{\bar{\nu}_{rot}} = 2B(1+1) - 4D(1+1)^3 = (4B - 32D) \text{ cm}^{-1}$$

$$\underset{J=2\rightarrow 3}{\bar{\nu}_{rot}} = 2B(2+1) - 4D(2+1)^3 = (6B - 108D) \text{ cm}^{-1}$$

Thus we see that the spectral lines are no longer exactly equal distance but their separation distance decreases with increasing value of J.

4 .9 Isotopic effects on the rotational spectra

The diatomic molecule having different isotopes of the same element, such as HCl, DCl, show different rotational spectra. This is because of the fact that masses of the isotopic atoms are different and hence the reduced mass, moment of inertia, as well as frequencies of rotation, would be different. It has been established that

$$B \ \alpha \ \frac{1}{\mu}$$

Thus, spectrum of heavier species will show smaller value of B and hence smaller separation between the spectral lines. This fact has been used in the evaluation of precise atomic weights.

The validity of the theory of rotational spectra can be tested by considering the example of carbon monoxide molecule:

The first rotational spectral line corresponding to the transition from J=0 to J=1 and appears at

$$\overline{V}_{rot} = 3.84235\ cm^{-1}$$ .We know that

$$\underset{J \rightarrow (J+1)}{\overline{V}_{rot}} = 2B(J+1)cm^{-1}$$

$$\therefore \underset{J = 0 \rightarrow 1}{\overline{V}_{rot}} = 2B(0+1) = 2Bcm^{-1} = 3.84235$$

$$\text{Hence } B = 3.84235/2 = 1.92118\ cm^{-1}$$

The moment of inertia of CO is given by-

$$I = \frac{h}{8\pi^2 CB} = \frac{6.624 \times 10^{-27}}{8 \times (3.14)^2 \times 2.9978 \times 10^{10} \times 1.92118}$$

$$= 1.45673 \times 10^{-39}\ gm.cm^{-2}$$

Reduced mass of CO will be

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{1}{N} = \frac{12 \times 15.9949}{12 + 15.9949} \times \frac{1}{6.023 \times 10^{23}}$$

Where m_1 = 12 gm (Carbon), m_2 = 15.9949 (Oxygen)

N = Avogadro's number = 6.023×10^{23}

$\therefore \mu = 1.138365 \times 10^{-23}$ grams per molecule.

The bond length of CO molecule can be calculated by the equation.

$$I = \mu r^2$$

Where I = moment of Inertia,

μ = Reduced mass of the molecule ,

r = Both length i.e., inter-nuclear distance between two atoms.

$$\therefore\ r_{co} = \left[\frac{1}{\mu}\right]^{\frac{1}{2}} = \left(\frac{1.456773 \text{ x } 10^{-39}}{1.138365 \text{ x } 10^{-23}}\right)^{\frac{1}{2}} \text{cm}$$

$$\text{Or,}\quad r_{co} = 1.131 \text{ x } 10^{-8} = 1.131\ \mathring{A}$$

This value of bond length of CO of molecule is in good agreement with the experimental value. This indeed is the most accurate determination of bond length. From rotational spectra we can also calculate the rotational energy at any level and the moment of inertia of the molecule.

Summary

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1) **Spectroscopy-** It is the branch of science which deals with the study of interaction of electromagnetic radiation with matter.
2) **Regions of the electromagnetic spectrum-** When different electromagnetic radiation arranged in order of their increasing wavelength or decreasing frequencies, the arrangement is called the electromagnetic spectrum. In order of wavelength.

   Cosmic rays< γ-rays< X-rays< UV rays< Visible light< IR< Microwaves

3) **Molecular spectroscopy-** When energy is absorbed by molecules, it may result into rotation, vibration or electronic transition. These energies have quantized values. The rotational, vibrational and electronic energy levels are called **"molecular energy levels"**. electronic energy levels have Quantum numbers, n=1,2,3,...., vibrational levels have v= 0,1,2… and rotational levels have J=1,2,3…. The transitions between these levels give **molecular spectrum.**
4) **Born-Oppenheimer approximation-** According to it, total energy of a molecule is the sum of transitional, rotational vibrational and electronic energies, i.e. $\mathbf{E=E_t+E_r+E_v+E_e}$. Further, translational energy is found to be negligible, hence the approximation used is $\mathbf{E=E_r+E_v+E_e}$.
5) **Selection rule-** A transition can take place only between definite energy levels. The restrictions thus applied are called selection rule. A transition which can take place is

called **“allowed transition”** whereas a transition which cannot take place is called **“forbidden transition”**.

Gross selection rules related to the feature that the molecule must have Where are specific selection rule are in terms of quantum numbers e.g **Δ J= ±1 or Δ ν = ± etc.**

6) **Intensity of spectral lines-** Intensity of a line means how strong or weak is the line. It depends upon-
   a) Population of states with particular energy (population density) initial state.
   b) Strength of the incident radiation.
   c) Probability that transition will take place between the energy levels. At any temperature T, ratio of populations of two states with energy E, and E’ is given by **“Boltzmann distribution law”**

$$\frac{N'}{N} = e^{-h\nu/kT} \qquad \text{Where, } h\nu = E' - E = \Delta E$$

7) **Pure-rotational (microwave) spectra of diatomic molecules-**

Some important features:-

   a) The quantized values of the energies of the rotational levels are given by.

$$E_j = \frac{h}{8\pi^2 I} J(J+1)$$

Where I= moment of inertia of the molecule and J is rotational quantum number (= 0, 1, 2, 3……..)

   b) **Isotopic effect-** if in a molecule, an atom is replaced by its isotope, then B = $\frac{h}{8\pi^2 I}$, I will change. If I, increases, B will decrease. As frequency separation= 2B, the energy levels will come closer.

Pure-Vibrational and Vibrational-Rotational Spectra of Diatomic Molecules (IR Spectra)-

Isotopic effect- Each line in the vibration- rotation spectrum of HCl is found to split into doublets. This is due to two isotopes of Cl which is ^{35}Cl and ^{37}Cl in HCl.

Raman spectra:

1) It deals not with the absorption but deals with the **“scattering”** of light by molecules. If scattered light is observed that right angles to the incident light, it is found to have,

a) Same frequency as that of incident light **(Rayleigh scattering)**

b) Lower frequency than that of incident light **(Stokes lines)**

c) Higher frequency than that of incident light **(Anti-Stokes lines)**

The differences $\Delta\nu = \nu_i - \nu_s$ is called “Raman frequency” or “Raman shift”.

2) Gross selection rule for the molecule to give rotational Raman spectrum is the polarizability of the molecule must be anisotropic i.e. polarizability of the molecule must depend upon the orientation of the molecule with respect to the direction of the electric field.

3) Specific selection rule for pure rotational Raman spectrum is that the polarizability of the molecule must be anisotropic i.e. polarizability of the molecule must depend upon the orientation of the molecule with respect to the direction of the electric field.

Advantages of Raman spectra over IR spectra:

1. They can be observed in the visible range.
2. They can be obtained for molecules like O_2, N_2, etc. which have no permanent dipole moment.
3. They can be obtained even for liquid and solids.

Electronic spectra:

1. When light is absorbed in the visible or ultraviolet region, electronic transitions take place accompanied by vibrational and rotational transitions. Groups of closely spaced lines are obtained called bands.
2. **For an electron transition:**

   $\Delta E = (E'c + E'\nu + E'r) - (Ee + E\nu + Er) = \Delta Ee + \Delta E\nu + \Delta Er$

   As, $\Delta E = h\nu = hc\bar{\nu}$, we have $\bar{\nu} = (Ee + E\nu + Er)/hc$

3. **Franck-Condon principle:** Nuclei being much more messive than electron, an electronic transition takes place very much faster than the nuclei can adjust to their new equilibrium position. If two electronic states are represented by their potential energy curves. Since inter-nuclear separation remains the same, transition is represented by their potential energy curves, since the inter-nuclear separation remains the same, transition is represented by a vertical line. There is no restriction (selection rules) for change in vibrational quantum number. All types of transition from lowest vibrational level to any of the vibrational levels of higher electronic state

are possible. Most probable transition is from v = 0 to v = 2 and has maximum intensity. Other transitions like; (zero) 0 → 0, 0 → 1, 0→ 3, 0 → 4 etc. have lower intensities.

Some selection rules for electronic transitions:

1. Only those transactions are allowed for which difference in component of Orbital angular momentum along Z-axis = 0 to1.
2. Transition are allowed only between states have some multiplicity.
3. Only those are transitions are allowed which are accompanied by change in parity.

Molecular orbitals involved in electronic transition:

Molecular orbital present in a molecule and involved in electronic transition are bonding orbital (σ and π), corresponding anti bonding molecular orbital (σ* and π*) and non bonding orbital (containing lone pair of electronic of heteroatoms like N, O etc, represented by 'n'.

The transition allowed $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$. The type of transition involved depends upon the nature of the compound or group present and takes place by absorption of suitable frequencies. The occurrence of colored compounds indicates absorption in the visible region. The groups present in such compound are called **"Chromophores"**.

Vibrational spectra

4.10 Brief idea about vibrational or infrared spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques which offer the possibility of structure identification. IR technique one couple with intensity measurements may be used for quantitative analysis. Infrared has been of tremendous used to chemists and his is currently more popular as compared to other physical techniques (x-ray diffraction, electron spin resonance, etc) in the elucidation of the structure of unknown compounds.

The range of infrared radiation:

The infrared radiation refers broadly to that part of the electromagnetic spectrum which lies between the visible and microwave regions. From instrumentation and application point of view the infrared region has been subdivided as follows:

a. The photographic region. this ranges from visible to 0.8 μ (1μ=10^{-3} mm or 10^{-4} cm)

b. The near infrared region (overtone region). it ranges from 0.8μ to 2.5 μ (12500-4000 cm^{-1}).It has energy is in the range 37 to 10 kcal $mole^{-1}$

c. The Mid Infrared Region (vibration rotation region). It ranges from 2.5 to 15 μ (4000-667 cm^{-1}). It corresponds to energies in the range 10 to 10 kilo cal $mole^{-1}$.

d. The far infrared region (or rotation region). This ranges from 15 to 200 μ (667-50cm^{-1}) and corresponds to energies in the range 1.0 to 0.1 kcal $mole^{-1}$. However, the reason of greatest practical use comprises The Limited portion between 4000 cm^{-1} to 667 cm^{-1} (2.5-15.0 μ)

An infrared spectrum shows the downward peak corresponds to absorption, plotted against wavelength (λ) or wave number ($\bar{\nu}$). Wavelength is expressed in (microns) or (1μm =10^{-1} cm). Since λ is inversely proportional to energy, the wave-number in cm^{-1} in is mostly used to measure the position of the given infrared absorption. This is due to the fact that wave number is directly proportional to energy ($E = hr = hc/ \lambda = hc\bar{\nu}$) of vibration.

4.11 Vibrational energy levels of a simple harmonic oscillator:

A simple harmonic oscillator is one in which restoring force is proportional to the displacement in accordance with hooks law i.e.

$$F= -kx \qquad ... ... (1)$$

Where, k is called the force constant.

For such an oscillator, the potential energy is given by:

$$= \frac{1}{2}kx^2 \qquad ......(2)$$

This is the equation for a parabola. Hence A parabolic potential energy curve is obtained as shown in fig.1.

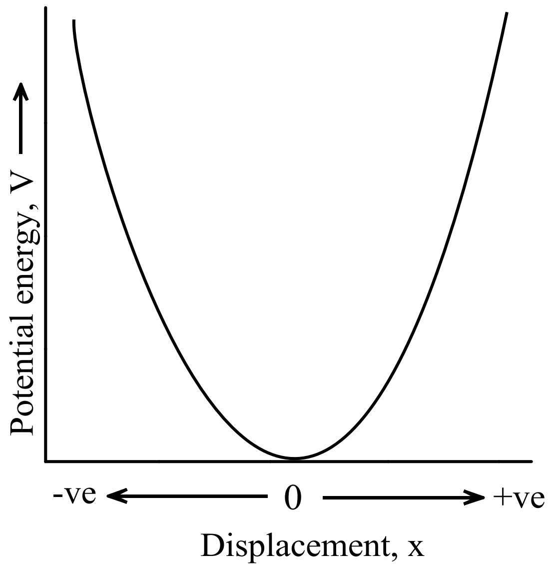


Fig. 1 Parabolic potential energy of a harmonic oscillator

Using the concept of quantum mechanics, it can be seen that if the vibratory motion of the nuclei of a diatomic molecule (Fig.2) is taken as equivalent to that of a simple harmonic oscillator, then the vibrational energy is given by equation.

$$E_v = \left(V + \frac{1}{2}\right) hr \qquad ……(3)$$

Where r is the frequency of vibration and v is a vibrational quantum number with allowed values of 0,1,2,3 etc

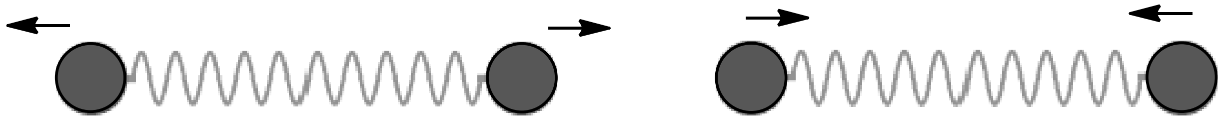


Fig. 2 Vibratory motion of a diatomic molecule

Putting $v = \frac{c}{\lambda} = c\bar{\upsilon}_e$ or $C\omega_e$* or where $\bar{\upsilon}_e$ or ω_e represents the equilibrium vibrational frequency in terms of wave numbers, equation (3) can be written as.

$$E_v = \left(V + \frac{1}{2}\right) hc\omega e \qquad \ldots\ldots(4)$$

Putting v=0, 1, 2, 3 etc. in equation (4) it may be seen that the vibrational energy levels of harmonic oscillator are equally spaced. These are shown diagrammatically in Fig.3.

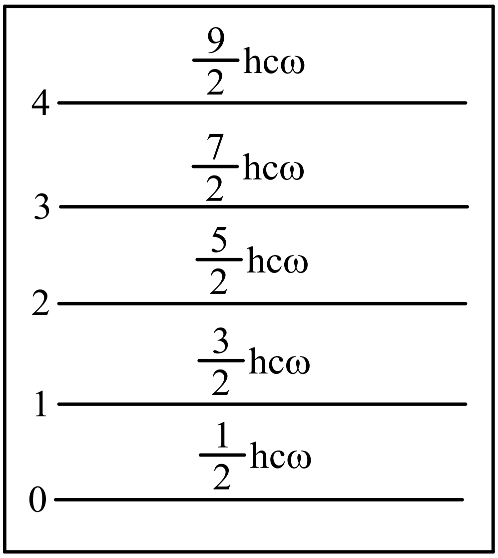


Fig. 3

For the lowest vibrational level, v=0. The energy for the level will, therefore, be

$$E_0 = \frac{1}{2} hc\omega_e \qquad \ldots\ldots(4)$$

This is called zero point energy. It implies that even at absolute zero when all translational and rotational motion ceases in a crystal, the residual energy of vibration E_o still remains, i.e., the vibrational motion still exists.

4.12 Selection rules for vibrational transitions in a simple harmonic oscillator

The gross displaced. Here not that the molecule need not have a permanent dipole. Based on this, the specific selection for rule for vibrational $\Delta v = \pm 1$ transition is i.e. Change in vibrational quantum number should be unity. Transitions for which Δν = ±1 corresponds to observe action and those with Δν = -1 response to emission.

* For a diatomic molecule, x=R-R_e , where R is distance to which the atoms have been stretched and R_e is equilibrium distance between the two atoms.

** υ is avoided because this is used to represent the frequency of the spectral lines.

4.13 Vibrational spectra of a simple harmonic oscillator

Applying selection rule, as the transition can take place between vibrational levels who is vibrational quantum numbers differ by Unity (i.e. Δν = ±1), the energy absorbed by a diatomic molecule, taking it as a simple harmonic oscillator, when the transition takes place from v to v+1 level will be given by:

$$\Delta E_v = \left(\nu + 1 + \frac{1}{2}\right) hC\omega_e - \left(\nu + 1 + \frac{1}{2}\right) hc\omega_e = hc\omega_e$$

$$\text{Or,} \quad \frac{\Delta E}{hc} = c\omega_e$$

$$\text{i.e.}\, \Delta\bar{\nu} = \omega_e$$

Thus, only one absorption line will be obtained in the vibrational spectrum whose wave number is equal to the equilibrium vibrational frequency of the diatomic molecule. Otherwise, too, as the vibrational levels are equally spaced, any transition from any v to v+1 will give rise to the same energy change and hence only one absorption line is expected. Further, at room temperature, as most of the molecules are in the lowest (ground state) vibrational level with v=0, therefore the transition taking place are v=0 to v=1. The frequency thus observed is called the fundamental frequency. The Spectra are observed in the infrared (IR) region.

4.14 Anharmonic oscillator concept (purely vibrational spectra)

The Schrodinger Wave Equation, on solving for anharmonic oscillator, gives the following expression for vibrational energy:

$$E_{vib} = \left[\left(\nu + \frac{1}{2}\right) h\nu_e - \left(\nu + \frac{1}{2}\right)^2 h\nu_e x\right] \text{ergs}$$

$$= \frac{1}{hc}\left[\left(\nu + \frac{1}{2}\right) h\nu_e - \left(V + \frac{1}{2}\right)^2 h\nu_e x\right] \text{cm}^{-1}$$

$$= \left[\left(\nu + \frac{1}{2}\right)\frac{\nu_e}{e} - \left(\nu + \frac{1}{2}\right)^2 \frac{\nu_e}{c} x\right] \text{cm}^{-1}$$

$$\text{E}_{\text{vib}} = \left[\left(\nu + \frac{1}{2}\right)\nu_e - \left(\nu + \frac{1}{2}\right)^2 \nu_e x\right] \text{cm}^{-1}$$

Where, ν_e = Equilibrium oscillation frequency (wave number),

x = Anharmonicity constant, it has small magnitude.

Selection rule:

Because of anharmonicity, the vibrational transitions are not confined to adjacent levels only, but many also occur between different levels. So that $\Delta\nu = \pm1, \pm2, \pm3...$

The above expression is the selection rule for harmonic oscillator regarding the vibrational transitions.

The transitions involving $\Delta\nu > 1$, however, would be less probable because at room temperature, only lowest vibrational level ($\nu = 0$) is occupied, and therefore, most of transition would originate from $\nu = 0$ level.

The energy changes, frequencies of lines from different transitions can be expressed as follows:

Transitions	ΔE_v	Frequencies

$\Delta v = +1$ i.e, $v = 0$ to $v = 1$ $0 \to 1$	$\Delta E_v = hv_{0 \to 1} = hV_e(1\text{-}2x)$	$V_{0 \to 1} = (1\text{-}2x)V_e$
$\Delta v = +2$ i.e, $v = 0$ to $v = 2$ $0 \to 2$	$\Delta E_v = hv_{0 \to 2} = 2hV_e(1\text{-}3x)$	$V_{0 \to 2} = (1\text{-}3x)2V_e$
$\Delta v = +3$ i.e, $v = 0$ to $v = 3$ $0 \to 3$	$\Delta E_v = hv_{0 \to 3} = 3hV_e(1\text{-}4x)$	$V_{0 \to 3} = (1\text{-}4x)3V_e$
$\Delta v = +1$ i.e, $v = 1$ to $v = 2$ $1 \to 2$	$\Delta E_v = hv_{1 \to 2} = hV_e(1\text{-}4x)$	$V_{1 \to 2} = (1\text{-}4x)V_e$

Each different vibrational transition will lead to separate line in the spectrum, with frequencies as indicated above,

a. The line appearing due to transition from v=0 → v=1 is called fundamental Band.

b. v=0 → v=2 transition games the line called first overtone Band (second anharmonic).

c. v=0 → v=3 transition produces the spectral lines called second overtone Band (third anharmonic).

d. v=0 → v=4 will correspond to third overtone (fourth anharmonic) etc. The intensity of these overtones keeps up on falling with the increase in the degree.

Hot bands:

At room temperature only, the lowest vibrational energy level (v = 0) is occupied. Thus most of vibrational transitions originate from level (v = 0). As the temperature rises, molecules migrate from lowest level to v = 1. Thus a sufficient number of molecules occupy level v = 1 at Higher temperatures, thereby permitting vibrational transitions to originate from v = 1. Such transitions from v=1 to higher levels reduce the spectral lines called hot bonds. As the temperature rises, the intensity of hot bonds increases

4.15 Intensities of the lines in P and R branches

It is important to note that intensities of the lines in P and R branches of the type shown in Fig.2 (b) will be observed only if the resolving power of the spectrometer is very high. If the resolving power is not so high, then the spectrum observed as shown in Fig.1.

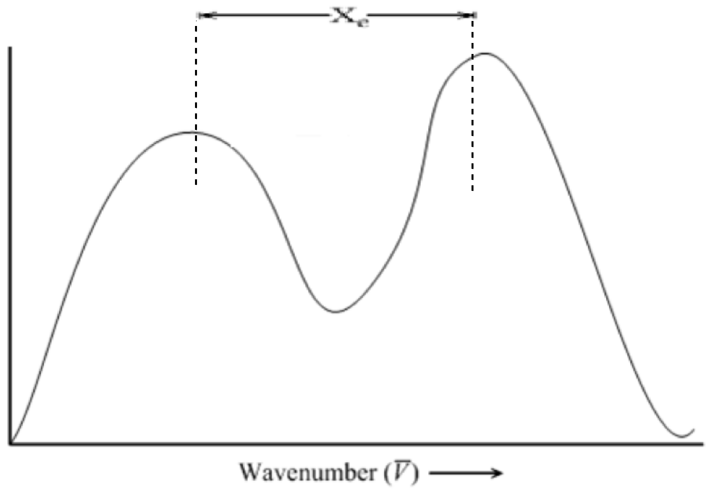
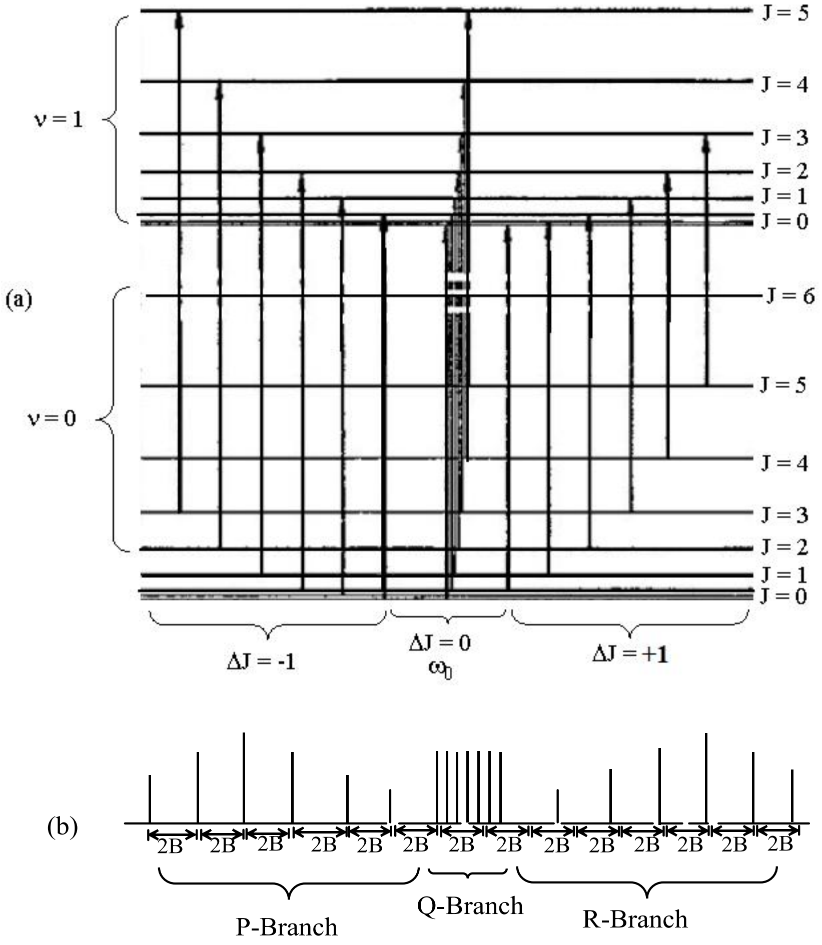


Fig.1. Vibration-rotation spectrum with low revolving power spectrometer



(a) Vibration-rotation spectrum of a diatomic molecule (b) Intensities of the lines.

4.16 Determination of force constant

Taking a simple case where a diatomic molecule may be considered as a simple harmonic oscillator i.e. on oscillator in which the restoring force (F) is directly proportional to the displacement, in accordance with hook's law, we have

$$F= -kx \qquad \ldots\ldots(1)$$

Where x is the displacement and is equal to the distance to which the atoms have been stretched (R) means equilibrium distance between the atoms (R_e) i.e $x=R-R_e$.k in equation (1) is called force constant. Thus if x = 1 cm, k= -F. Hence force constant may be defined as restoring force per unit displacement (or per cm) of harmonic oscillator. It is found to be related to the equilibrium vibrational frequency ω_e according to equation,

$$\omega_e= \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \ldots\ldots(2)$$

Where μ is reduced to mass of the system.

To calculate k, equation (2) can be rewritten as follows:

$$k= 4\pi^2\omega_e^2\mu$$

$$k= 4\pi^2\omega_e^2 \frac{m_1 m_2}{m_1+ m_2} \qquad \ldots\ldots(3)$$

Where m_1 and m_2 are masses of the oscillating atoms.

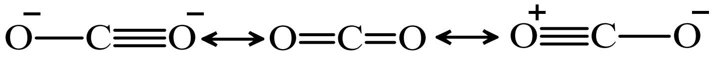
Thus knowing vibration frequency ω_e and the mass of the atoms of the diatomic molecule, the force constant k can be calculated. Note that ω_e it is in S^{-1}.

However, a problem arises with polyatomic molecules, because each bond has a different force constant. This problem is solved by assuming that a force constant is associated not only with every bond but also with every bond angle. A detailed study of such molecules is beyond the scope of present book.

The force constant for number of bonds have been determined. It is found that force constants increase almost directly with the multiplicity of the bond. This is illustrated by some values given below:

Bond	Force constant (dynes/cm)
$C-C$ $C=C$ $C\equiv C$	4.6×10^5 9.5×10^5 15.8×10^5

Thus the multiplicity of the bond can be predicted from the value of the force constant. For example, the force constant for C=O or in carbon monoxide is 18.6×10^5 dynes/cm where as the force constant for C=0 in carbon dioxide is 15.2×10^5 dynes/cm. This result confirms that CO_2 resonating structures containing both carbon oxygen double and triple bonds i.e. we write



$$\overset{-}{O}-C\equiv\overset{-}{O}\longleftrightarrow O=C=O\longleftrightarrow\overset{+}{O}\equiv C-\overset{-}{O}$$

Raman spectrum

4.17 Brief idea about Raman spectrum

It is a special type of Spectroscopy which deals not with the absorption of electromagnetic radiation but deals with the scattering of light by the molecules. it is observed that when a substance which may be gaseous, liquid or even solid is irradiated with monochromatic light of a definite frequency is, a small fraction of the light is scattered. Rayleigh found that if the scattered light is observed at right angles to the direction of the incident light, the scattered light is found to have the same frequency as that of incident light. This type of scattering is called Rayleigh scattering.

Professor C.V. Raman of Calcutta University, however, observed in 1928 that when a substance (gaseous, liquid or solid) is irradiated with a monochromatic light of a definite frequency ν, the light scattered at right angles to the incident light contains lines not only of the incident frequency but also of lower frequency and sometimes of higher frequency as well. The lines with the lower frequency are called Stokes' line whereas lines with higher frequency are called anti Stokes' lines. Raman further observed that the difference between the frequency of the incident light and that of a particular scattered lines was constant depending only upon the nature of the substance being irradiated and was completely independent of the frequency of the incident light. If ν_i is the frequency of the incident light and ν_s, that of particular scattered line, the difference $\Delta\nu = \nu_i - \nu_s$ is called Raman frequency for Raman shift.

Thus the Raman frequencies observed for a particular substance are characteristic of that substance.

The various observations made by Raman Institute what is called Raman Effect and the spectrum observed is called a Raman spectrum. Thus in a simple way, Raman spectrum may be represented as shown in fig.1.

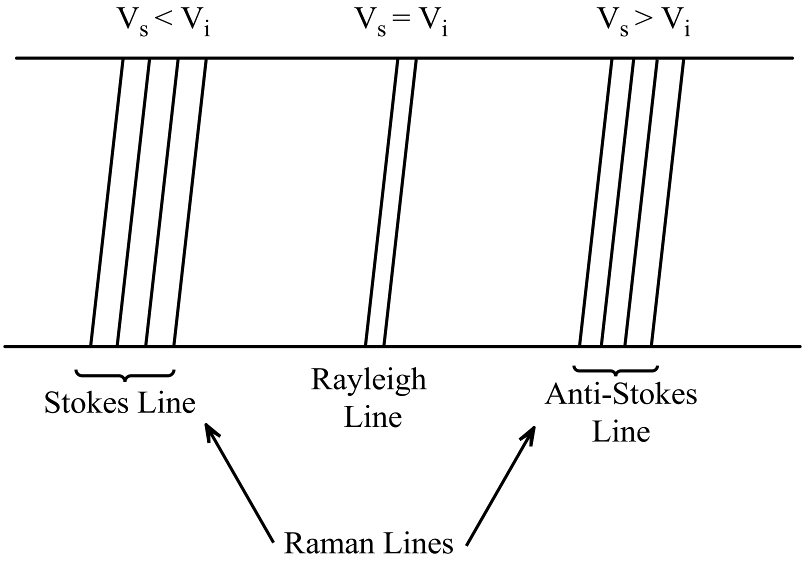


Fig.1. A simplified representation of Raman spectrum.

4.18 Concept of Polarizability (Classical Theory of Raman Effect)

Classical theory is able to explain the existence of the effect by Quantum theory is required to predict selection rules and intensities correctly. When an electric field is applied to a molecule its electrons and nuclei are displaced i.e., the electrons are attracted to the positive pole while the nuclei to the negative pole. An induced dipole moment is thus produced in the molecule due to the displacement of the electron and nuclei and the molecule is said to be polarized. Suppose F is the strength of Electronic field, μ is the magnitude of induced moment, and then we can write

$$\mu = \alpha F \qquad \text{........(1)}$$

Where, 'α' donates the polarizability of the molecule. The strength F of the electronic field of an Electromagnetic wave of a frequency ν maybe put as

$$F = F_0 \mathrm{Sin} 2\pi\nu t \qquad \text{........(2)}$$

Where F_0 is the equilibrium value of field strength. On combining equation (1) and (2), we get

$$\mu = \alpha F_0 \mathrm{Sin} 2\pi\nu t \qquad \text{........(3)}$$

From equation (3) it follows that the interaction of electromagnetic waves of frequency ν induces in the atom or molecule a dipole which oscillates with the same frequency. According to classical theory this oscillating dipole would emits radiation of the same frequency ν, i.e., incident and scattered frequencies will be same; this is the case of Rayleigh’s scattering. While reducing equation (3), vibration and rotation of molecules have not been considered. We will now consider the effect of vibration and rotation on equation (3).

Effect of vibration:

Suppose we are considering the diatomic molecule. As the two nuclei of the diatomic molecule vibrate along the line joining them, the polarizability of the molecule will change. If x is the small displacement from the equilibrium position, the vibration is polarizability, α is given by,

$$\alpha = \alpha_0 + \beta \frac{x}{A} \qquad \text{........(4)}$$

Where α_0 is known as equilibrium polarizability, β denotes the rate of vibration polarizability with distance and A is the vibration amplitude. Suppose the molecule executes simple harmonic motion. Then the displacement, it x, can be put as

$$x = A \mathrm{Sin} 2\pi U_v t \qquad \text{........(5)}$$

Where U_v denotes the frequency of the vibration of the molecule. On substituting equation (4) in (3). We get

$$\mu = \alpha_0 F_0 \mathrm{Sin} 2\pi\nu t + \beta F_0 \mathrm{Sin} 2\pi\nu t \, \mathrm{Sin} 2\pi U_v t$$

$$= \alpha_0 F_0 \mathrm{Sin} 2\pi\nu t + \frac{1}{2}\beta F_0 [\mathrm{Cos} 2\pi(\nu - U_v)t - \mathrm{Cos} 2\pi(\nu + U_v)t] \quad \text{......(6)}$$

Thus, the induced dipole oscillates with frequencies ($U+U_v$) and ($U-U_v$) which more than the frequency of incident radiation and predicts the existence of Raman scattering.

Thus, the Raman shift will be as follows:

$$\text{Raman Shift} = (U - U_v) - U = U_v$$

From equation (6A) it follows that Raman shift will be equal to the frequency of vibration of diatomic molecule.

Effect of rotation:

As far as the effect of rotation of molecule on polarizability is concerned, when a diatomic molecule rotates the orientation of a molecule varies with respect to the electric field of rotation. If the molecule is not optically isotropic i.e., it exhibits different polarizabilities in different directions then its polarization will vary with the time. If we express variation of α by an equation, identical to equation (5), we have-

$$\alpha = \alpha_0 + \beta'\text{Sin}2\pi(2U_r)t \qquad ....(7)$$

Where U_r is the frequency of rotation. In the above equation, where $2U_r$ has been put instead of U_r because of rotation through Pi angle will bring the diatomic molecule in a position in which its polarizability becomes same as initially. On substituting equation (7) into (5), we get-

$$\mu = \alpha_0 F_0 \text{Sin}2\pi Ut + \beta' F_0 \text{Sin}2\pi Ut\ \text{Sin}4\pi U_r t$$

$$= \alpha_0 F_0 \text{Sin}2\pi Ut + \frac{1}{2}\beta F_0[\text{Cos}2\pi(U - 2U_r)t - \text{Cos}2\pi(U + 2U_r)t] \quad ......(8)$$

From the above equation it follows that the frequency of a Raman lines will be $(U+2U_r)$ and $(U-2U_r)$ .in this case, the Raman shift would be

$$\text{Raman Shift} = (U + 2U_r) - U = 2U_r \qquad ......(8A)$$

From equation (8A) it follows that the Raman shift would be equal to twice the frequency of rotation of molecule.

4.19 Pure rotational Raman spectra of diatomic molecules

The selection rule for rotational Raman spectra is ΔJ = 0, ±2 which is different from the selection rule in infrared spectroscopy. When ΔJ = 0, the scattered Raman radiation will be of the same frequency as that of incident light (Rayleigh scattering). The transitions ΔJ = ±2 gives Stokes lines (longer wavelengths) where ΔJ = -2 gives to anti-stokes lines (shorter wavelengths). Utilizing the relation for the energy of rigid rotator,

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

Where ΔJ = ±2, the value of rotational Raman shifts (Stokes line) will be given by-

$$\Delta\bar{\nu} = \frac{h^2}{8\pi^2 I_c} \{(J+2)(J+3) - J(J+1)\}$$

$$\Delta\bar{\nu} = 2B(2J+3) \quad \text{Where } B = \frac{h^2}{8\pi^2 I_c} \qquad ......(2)$$

When (fig), the values of rotational Raman shifts (anti Stokes lines) will be given by-

$$\Delta\bar{\nu} = 2B(2J+3) \qquad ......(3)$$

On combining equations (2) and (3) the Raman shift can be put in the form

$$\Delta\bar{\nu} = 2B(2J+3) \quad \text{Where } J = 0, 1, 2, ...$$

The wave number of corresponding spectral lines will be thus, given by-

$$\bar{\nu} = \bar{\nu}_{ex} + \Delta\bar{\nu}$$

Where Vex is the same wave number of exciting radiation.

The transitions and the Raman spectrum arising from there are in drawn schematically in Fig.1.

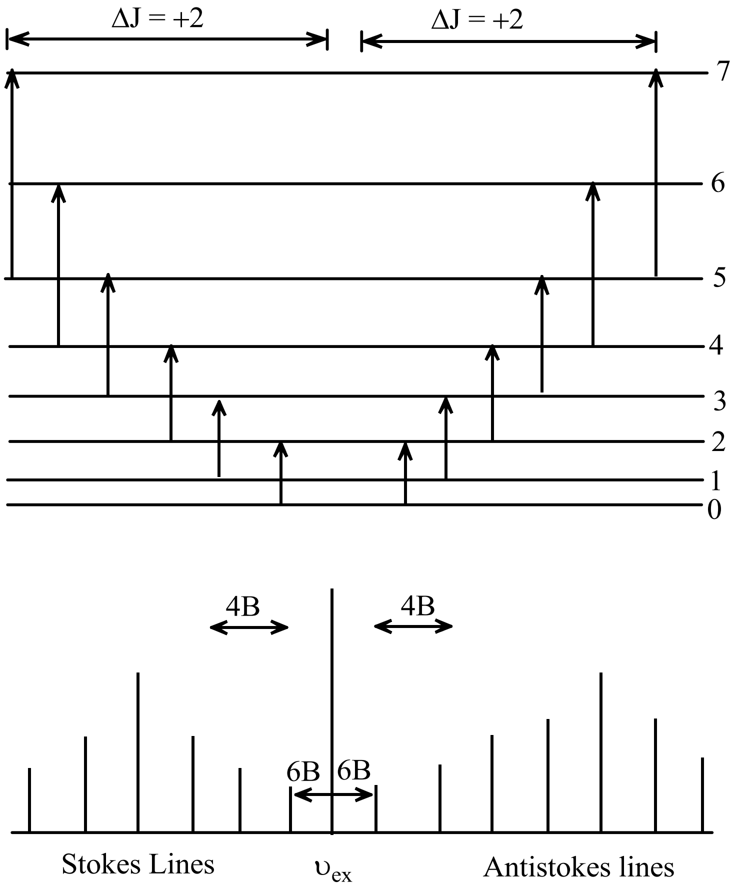


Fig. 11: Rotational energy levels of a diatomic molecule and the rotational Raman spectra

From the figure 1 it can be seen that frequency separation of successive lines is 2B cm^{-1} where as it is 4B cm^{-1} in the far infrared spectra. While on substituting J = 0 in equation (4) we deserve that the separation of the first line from the exciting line will be 6B cm^{-1}. The homo-nuclear diatomic molecules (e.g. O_2 and H_2) do not exhibit infrared or microwave spectra but they do exhibit rotational Raman spectra. Therefore, their structures can be ascertained. If a molecule possesses a centre of symmetry (e.g. H_2, O_2 and CO_2) the effect of nuclear spin will be observed in Raman as well as in the infrared spectra. Thus in O_2,CO_2 etc every alternate rotational level will be missing from the spectrum Fig.1 in the case O_2, CO_2 of etc. every alternate rotational level will be missing from the spectrum Fig.1 in the case O_2, energy level with even J values is missing (J=0,2,4,...)

4.20 Pure vibrational Raman spectra of diatomic molecules

If the diatomic molecule is treated as a simple harmonic vibrator then the vibrational energy E_v is given by-

$$E_v = \left(V + \frac{1}{2}\right) hc\omega$$

Where ν is the vibrational quantum number having values 0, 1, 2..., ω is the vibrational frequency, c. the velocity of light it and h is the Planck's constant.

The selection rule for a transition is Δν = ±1 but in practice only one value Δν = ±1 transitions are observed. When ν=0 is the initial level, a Stokes line is obtained. When ν' = ±1 and is the initial level, an anti-stokes line results.

Thus, the change in vibrational energy ΔE_v is given by-

$$\Delta E_v = E_v - E_v''$$

$$= \left(\nu' + \frac{1}{2}\right) hc\omega - \left(\nu'' + \frac{1}{2}\right) hc\omega$$

$$= (\nu' - \nu'')hc\omega$$

$$= \Delta\nu . hc\omega$$

$$= hc\omega$$

(Since Δv= ±1 by selection rule)

$$\Delta E_v = hc\omega = hc\Delta\bar{\nu}$$

Where $\Delta\bar{\nu}$ is the difference in Wave number of the observed Raman line from that of the exciting line. Stokes lines are more intense majority of the molecules are in the v=0 level at room temperature.

Electronic spectrum

4.21 Brief ideas about electronic spectrum

The electronic spectra are studied both in emission and absorption. The molecular spectra which appear in the UV region arise due to transitions of an electron from one electronic state (energy level) to another. On the other hand, the return of an excited molecule to lower electronic state, energy is released, leading to emission spectra. The electronic spectra involve large amount (it10^2 Kcals/mole) of energy change. Hence such spectra are found in UV or visible region. During electronic excitations vibrational and rotational transitions would also occur. Hence they are very complex in nature and each Bond in electronic spectra consists of a number of fine lines due to simultaneous changes in vibrational and rotational energies.

In spite of the complex nature of electronic spectra has many advantages over the microwave and infrared spectra like in case of homonuclear molecules, the dipole moment is zero, hence they do not give mid-infrared or a microwave spectra. But they (homonuclear molecules) show electronic spectra.

4.22 Concept of potential energy comes for bonding and anti-bonding MO

The explanation of electronic Bond spectra and dissociation energy can be easily understood in terms of potential energy gives as follows:

The potential energy curve of a diatomic molecule is obtained by plotting the potential energy of the system versus inter-nuclear distance between the two approaching atoms. The curve obtained is of the shape shown in Fig.1. However, even at the minimum energy position (equilibrium Fig.1 potential energy curve for a position), represented by point X, the diatomic molecule atoms are vibrating (so that the inter-nuclear distance keeps on changing), therefore the potential energy keeps on oscillating about the minimum position. The vibrational levels thus occupied by the system may be represented by horizontal lines and indicated by appropriate vibrational Quantum numbers. If sufficient energy is supplied so that system occupies the vibrational level represented by V_d, the corresponding inter-nuclear distance should become infinity i.e., the molecule should dissociated into atoms.

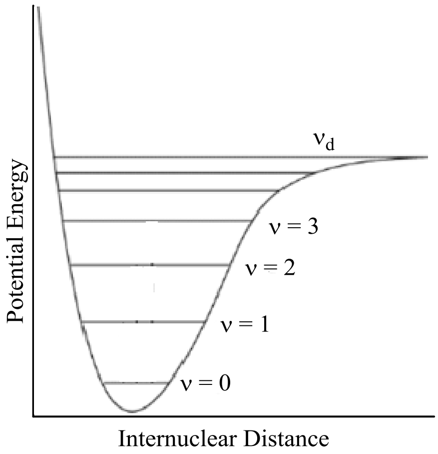


Fig.1. Potential energy curve for a diatomic molecule

However, this usually does not happen because before this stage is reached, the electron jumps into higher energy level i.e. electronic transition take place and the dissociation will take place only of the molecule in the higher energy level.

Now every electronic state has its own potential energy curve. Two such curves for the lower electronic states are shown in Fig.2 by I and II respectively. They differ in the fact that the minimum of the potential curve for the excited state (II) is at a larger inter-nuclear distance then the ground electronic state (I). The dissociation energies for the two states are different as shown in Fig.2. i.e. $D_2 < D_1$. This is evidently due to the fact that the bonding in excited state is weaker than the ground state. The vertical distance between the minima of the two curves gives the difference between the electronic energy of the two states. (ϵ_{el} as shown in Fig.2.)

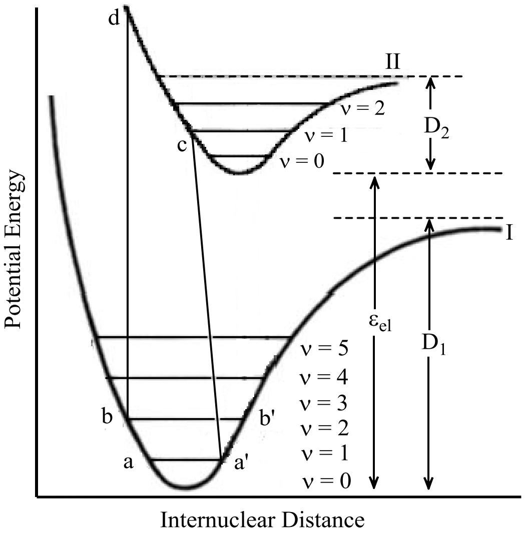


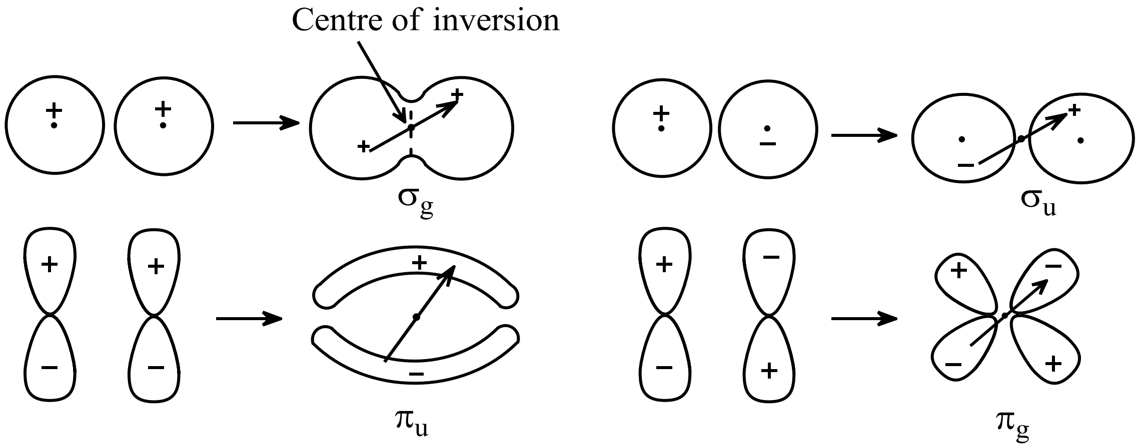
Fig.2. Electronic transitions in diatomic molecules.

4.23 Qualitative descriptions of selection rules

In order to understand selection rules for electronic transition in molecules, we should first understand a few terms and symbols to be used therein.

1. **Parity:**

   Parity represents the behavior of an orbital with respect to inversion. It is used for Molecular orbitals of nuclear diatomic molecules. We consider a point in the molecular orbital and note the sign of the orbital (wave function). Then we travel equal distance to the centre of the molecule to a point (centre of inversion) on the other side. (This operation is called inversion). If at this point, the orbital has the same sign, it is said to have even parity and is denoted by ‘g’ (from gerade, German would for even), then it is said to have odd parity and is denoted by ‘u’ (for angerade, uneven). The parity designations apply only two nuclear diatomic molecules because hetero-nuclear diatomic molecules (like HCl) do not have centre of inversion. As shown in Fig.1 below, a bonding Sigma orbital has even parity and is written as σ_g and antibonding σ (σ*) orbital has odd parity and is written as σ_u. A bonding π orbital has odd parity and is denoted as π_u and a π^* orbitals has even parity and is denoted by π_g.



Parity of an orbital is given (symbol ‘g’) if an inversion through the centre of symmetry, signing of orbital remains same. If sign changes, parity is odd and symbol is ‘u’.

2. Multiplicity of state: the ground state of any species may have one or more unpaired electrons with spinning in the same direction or opposite direction. If S represents total spin quantum number, then 2S + 1 give the spin multiplicity of the state. If S=0, multiplicity of state = 1. It is called singlet state. If S $=1/2$, multiplicity = 2 x $^1/_2$ + 1= 2. It is a doublet state. If S = 1, multiplicity = 3. It is called triplet state and so on. For example, in the ground state, H_2^+ has only one electron, its multiplicity = 2. Similarly, O_2 molecule in the ground state has a two unpaired electrons with parallel spins, its multiplicity = 3.
3. Term symbols of molecules: the symbols give complete information about the state of the molecule i.e. orbital angular momentum, multiplicity and parity.

Depending upon the component of the total angular momentum about inter-nuclear Axis, they are given the symbols Σ, π, Δ etc as follows:

Component of total orbital angular momentum about inter-nuclear axis:

Symbols: Σ π Δ

To the above symbols, multiplicity is added on the left as a superscript and parity is added as a subscript on the right. For example:

a. The single electron of H_2^+ in σ molecular orbital has zero orbital angular momentum. Hence the term symbol is Σ. Further, it has multiplicity = 0 (as explained earlier) and then parity of the only occupied orbital is g*, therefore full term symbol is $^2\Sigma_g$.

b. The term symbol for any closed shell homo-nuclear diatomic molecule is $^1\Sigma_g$ because the spin is 0 (as all the electrons are shared, there is no orbital angular momentum from a closed cell and the overall parity is g).

c. If there is only π electron outside a close the shell, its orbital angular momentum about the inter-nuclear axis = 1 unit. Hence the term symbol is π.

If there are two π electrons (as in O_2), the term symbol maybe Σ or π. The term symbol Σ will be used if the electrons are orbiting in opposite direction which can be so if they occupy different orbitals. The term symbol π will be used if the two π electrons are orbiting in the same direction which can be so if they occupy the same π orbital.

In case of O_2, of the ground state, the two electrons occupy different orbital's with parallel spin and the overall parity of the molecule = (closed shell) x g x g = g.

Hence that term symbol is $^3\Sigma_g$.

Lastly, a superscript '+' or '-' on an Σ term symbol is added to show the behavior of the molecular wave function on reflection in a plane containing the nuclei. In case of O_2, one electron is in 2πx which changes sign on a reflection in the yz-plane and the other is in 2πy which does not. The overall reflection symmetry is, therefore-

$$(\text{Closed shell}) \times (+) \times (-) = -$$

Hence the full term symbol is $^3E_g^-$.

Now, we get the below the selection rules for transitions between two different states of the molecule:

1. Only those transitions are allowed between the state for which the difference in the component of the orbital angular momentum along the Z axis=0, ±1. Thus $\Sigma \rightarrow \Sigma$, $\pi \rightarrow \Sigma$, $\Delta \rightarrow \pi$ transitions are allowed but $\Delta \rightarrow \Sigma$ is not allowed.
2. The transactions are allowed only between the states having same multiplicity. The singlet and triplet transitions may occur but singlet-triplet transitions are forbidden.
3. $\Sigma^+ — \Sigma^+$ transitions are allowed but $\Sigma^- — \Sigma^-$ not allowed.

4. Only those transactions are allowed which are accompanied by change in parity. Thus, g ↔ u and u ↔ g is allowed but g ↔ g and u ↔ u transitions are forbidden.

This is known as Laporate selection rule.

★ Is there are several electrons, the overall parity is calculated using the method g x g = g, u x u = g, u x g = u.

The rule has been generated by taking g = +1 and u = -1.

4.24 Franck Condon Principle and Intensities of Electronic Transitions

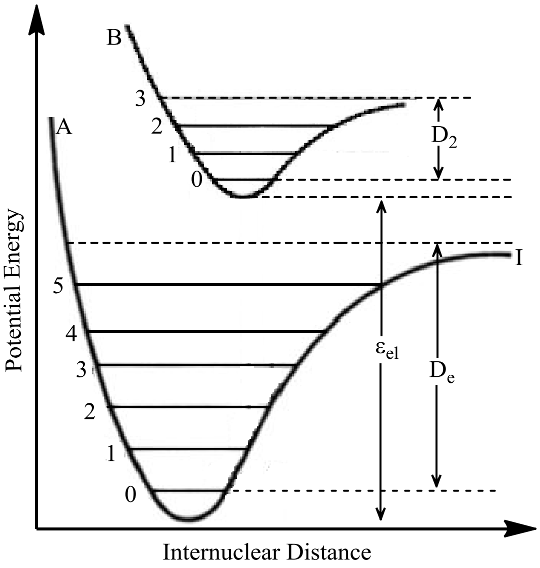
Every electronic state of a molecule has its own potential energy curve. Two such curves for a lower electronic state A and an upper electronic state B are drawn in Fig.1.

The nuclear separations at the minima of the curves are different in the Two States A and B, and so on also are the heats of dissociation. The vertical distance between the minimum of the two curves is equal to the difference in the electronic energy, E_e of the two states. However, the probability of the transition from a given vibrational level in the state A to any level in the state B, when the radiation is absorbed or a method is given by a rule first stated by Frank and later developed by Condon. This is commonly referred to as a Franck-Condon principle.

In essence this principle states that:

“The time required for an electronic transition to occur is so short as compared to the time required for one cycle of vibration that the inter-nuclear distance of the vibrating molecule does not undergo appreciable change during the transition.”

Since the time (10^{-15} secs) required for an electronic transition is very small compared with the time (10^{-13} secs) necessary for the nuclei to oscillate, the inter-nuclear distance will remain virtually constant during the course of an electronic change. This means that electronic transition will be represented by vertical lines only. If the inter-nuclear distance would have been changed in the upper level.



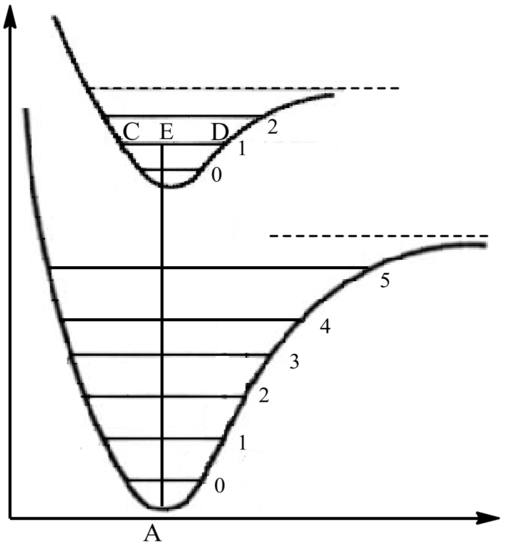


Fig.2

Fig.1

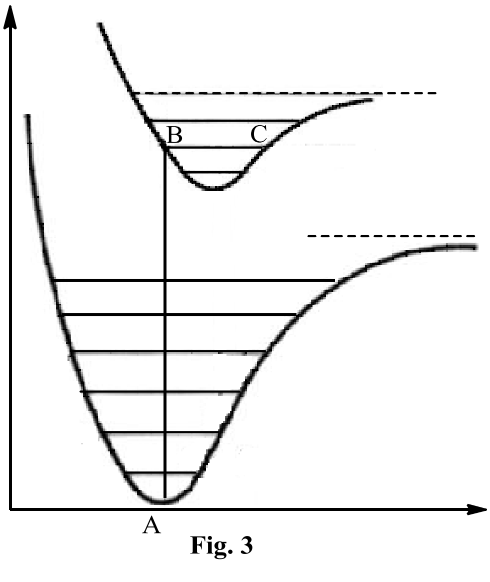


Fig. 3

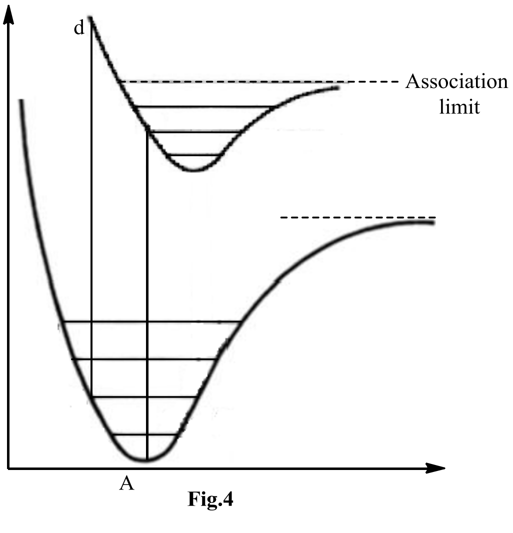


Fig.4

then the transition can be represented by slanting lines, but the nucleus does not change at all, so the only transitions that take place are in the vertical direction. This is the explanation of a Franck-Condon principle. In order to apply this principle we have to consider fig.2, 3,4.

In, the potential curve, the potential energy curves were you made by Franck Condon, for the upper and lower electronic states in the three typical cases of intensity distribution.

In figure to the potential curves of the two electronic States have been so chosen that their minimal live very nearly one above the other. This is the case of equal internuclear distance. In absorption the molecule is initially at the minima of the lower potential curve. It can be seen that for a transition to the minima of the upper potential curve (O — O) bond, the requirement for the Franck Condon principle is satisfied. On the other hand, a transition into a higher vibrational state CD would be possible only when, at the moment of the electronic jump either the position (transition from A to C) or velocity (transition from A to E) or both alter to an appreciable extent. At the point E, the molecule has the amount of kinetic energy EB. But at the point C or D, the kinetic energy and the velocity is zero. Thus, on the basis of Franck-Condon principle, a transition from $v''= 0$ to such a high vibrational level is forbidden. For the level $v' = 1$, the alteration of position or velocity during electrons jump is comparatively small. Therefore,

l→O bond will still appear with much smaller intensity then the O →O bond.

For the 2→0, 3→0 etc bonds, the necessary alterations of a position and velocity increase and rapidly decreasing of the position is observed. Thus, we obtain and intensity distribution of the type illustrated in figure (2).

Considering figure 3, the minimum of the upper potential curve lies at a somewhat great re value than that of the lower state. Therefore, a transition from minimum to minimum (0→0) band is no longer most probable, since the inter-nuclear distance must alter in such a transition. The most probable transition is that of a vertically upwards that is from A to B as shown in figure (3). For this transition, there is no change in the inter-nuclear distance at the moment of the jump.

Thus, immediately after the electron jump, the two nuclei still have their old distance from each other. Since the equilibrium inter-nuclear distance has a different value in the new electronic state, the nuclei start vibrating between B and C. The vibrational levels whose left turnings points lie in the neighborhood of B are the levels of the most intense bonds. For still higher vibrational levels, an appreciable change of inter-nuclear distance must take place, as a result of which the intensities of the bonds decrease again with the increasing v'. Thus the observed intensity distribution in the second case is explained.

In the next figure 4, the minimum of the upper potential curve lies at a still greater inter-nuclear distance. The Franck Condon principle is strictly fulfilled for the transition AB. The point P on the upper potential curve corresponds to the continuous region of the vibrational spectrum of the upper state. After such an electron jump the atoms will fly apart. The transitions to somewhat below, that is, in the discrete region and somewhat above B, that is, in the continuous region, are also possible. In this matter third case of intensity distribution is explained. Summarizing all these, we can say that in absorption, the most intense transition from v''=0, is always that corresponding to a transition from the minimum of the lower potential curve vertically upwards.

Now the three typical cases of intensity distribution in absorption Bond series are represented schematically in figure 5.

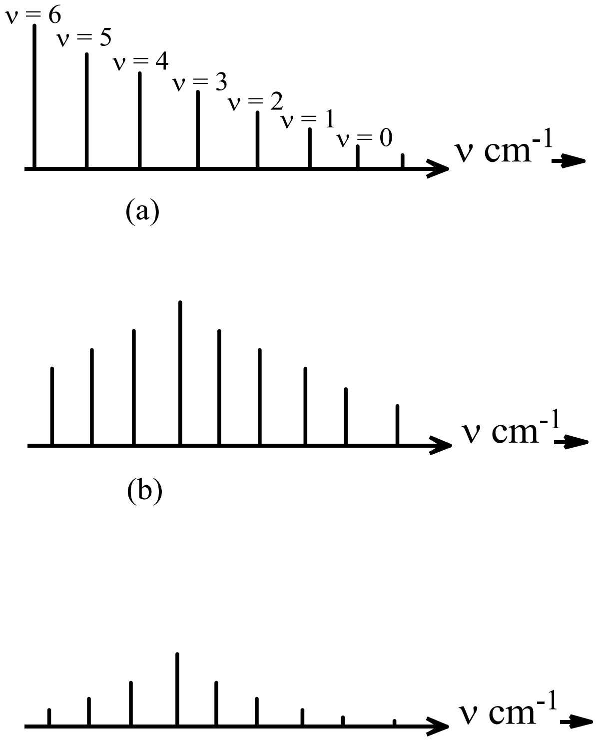


Fig.5

In the first case, 5(a), coming from long wavelengths, the 0 → 0 the band of the system is more intense. A few further bonds of the v''= 0 progression joining to it appear with rapidly decreasing intensities. In the second case 5(b), the intensity of bands in the progression v'' = 0, at first increases somewhat with the decreasing wavelength and then decreases slowly. In the third case 5(c) there is along progression of absorption bands whose intensity rises gradually from zero at the long wavelength end. The first observed band is usually not the (0 → 0) bond. Towards the shelter wavelengths, the bands draw closer together until they come to a convergence limit, at which continuum joins on. The maximum to the intensity lies at very high v’ values or possibly even in the continuum.

Wave mechanical formulation of Franck Condon principle:

Of wave mechanical treatment confirms in a General way the basic assumption of the Franck-Condon principle that a transitions vertically upwards or downwards in the potential energy diagram corresponds to the most intense bands. However, according to wave mechanics, an oscillator in the lowest vibrational level has the probability density distribution. Therefore, transition vertically upwards starting from v''=0 main take place with a certain range of re values. this consideration makes it quite clear as to why instead of only one band and nuclear bands of the v' progression with v''=0 appear in absorption, with a more or less broad intensity maximum.

As illustrated in figure 6 the vibrational eigen functions of the upper and lower states are bell-shaped curves. The more the minima are separated, the smaller is the overlap integral and, therefore, the smaller is the intensity of (0 → 0). If the minima of the two potential curves lie at equal inter-nuclear distance, the values of the overlap integral by large for the (0→0) band is quite small for the (1-0) band. If we know imagine the potential curve for the upper state to be shifted to larger or smaller re values, the integral and, therefore, the intensity of (1→0) band at first increases where as it decreases for the (0→0) band. The integral has a maximum value then the maximum (or minimum) of the upper Eigen function lies vertically above the lower Eigen function. At the same time, the overlap integral for the (0→0) band is smaller, if re if values of the minima of the potential curves differ still more, the overlap integral for the (0→1) band, and, therefore, the intensity of the (1→0) band decrease again. Entirely similar considerations apply to the (0→1) band.

4.25 Qualitative descriptions of σ, π and η molecular orbital's

All organic compounds are capable to absorbing electromagnetic radiations because all contain valence electrons that can be excited to higher energy levels. The electrons that contribute to absorption by an organic molecule are

1. In that participated directly in bond formation between atoms.
2. Non-bonding or unshared outer electrons that are localized about such atoms as oxygen, sulphur, nitrogen and the halogens.

The molecular orbital's associated with single bonds in organic molecules are designated as Sigma orbital's and the corresponding electrons are Sigma electrons. The double bond is an organic molecule contains (i) a σ-orbital corresponding to one pair of the bonding electrons and (ii) a π-molecular orbital associated with the other pair. π-orbitals are formed by the parallel overlap of atomic p-orbitals. Their charge distribution is characterized by a nodal plane (a reason of low electron density) along the axis of the bond and maximum density in regions below and above the plane.

Many organic compounds also contain non bonding electrons. These unshared electrons are designated by the symbol n. an example showing that three types of electron in an organic molecule is shown in Fig.1

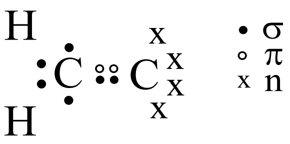


Fig.1 Different molecular orbital's in HCHO.

Energies for different types of molecular orbitals differ considerable E and order is:

$$E_{\sigma^*} > E_{\pi^*} > E_n > E_\pi > E_\sigma$$

4.26 Energy levels of σ, π, η and electronic transitions

In the ultraviolet and visible region following transitions are possible as shown in Fig.1

(fig)

1. An electron in an σ bonding orbital of a molecule absorbs radiation and is excited to the corresponding anti-bonding orbital. The energy required to induce a σ→σ* transition is large.

   Methane (CH_4) contains only simple C — H bonds and can undergo only σ →σ* transition. It exhibits and absorption maximum at 125 mm. Ethane also involves the same type of transitions. Here electrons of the C — C bond also appear to be involved. Strength of the C — C the bond is less than that of the C — H bond therefore less energy is required for excitation and thus, the absorption peak occurs at a longer wavelength i.e. 135nm. Propane, cyclohexane etc. all display σ → σ* transitions and their Sigma max are below 140nm.

2. **n → σ* transitions:**

   Saturated compounds containing items within shared electron pairs (non bonding electrons) exhibit n → σ* transitions e.g. CH_3OH, H_2O etc. These transitions require less energy than σ — σ* type. Methanol shows absorption at 184 nm while H_2O and isobutane show peaks at 167 and 257 nm respectively.

3. n → π* and π → π* transitions:

   Transitions between non bonding atomic orbitals and anti-bonding orbitals are called n → π* transitions. These transition occur with compounds containing double bonds e.g. C=0, C=S, N=0 etc. This type of transition is frequently observed in the spectra of aldehydes and ketones.

   Transitions between bonding π and anti-bonding π* are called π → π* transitions. These transitions occur in compounds containing conventional double or triple bonds, aromatic rings and carbonyl groups.

   Aldehydes and ketones exhibit two bonds: a more intense bond at 180-200 nm corresponding to π → π* transition and a low intensity n → π* transition at 280nm.

4.28 Terminal questions

1. What do you mean by selection rules in spectroscopy?
2. Explain why molecules behave as non rigid Rotors.
3. What are the factors which affect the intensity of spectral line?
4. What type of molecules exhibit vibrational spectra?
5. Out of H_2, O_2, N_2, HCl, CO, NO_2, CO_2, H_2O and CH_4 which will give a pure vibrational spectrum?
6. On the basis of the polarizability, explain which type of molecules will be rotationally Raman active and which will be inactive.
7. Why CO_2 is both IR and Raman active?

4.29 Questions and their Answers

Numerical

Example 1- the pure rotational spectrum of gaseous HCL is having a series of equal space the lines which are separated by 20 cm^{-1}. Find the inter-nuclear distance of the molecule. The atomic masses are ‘H= 1.673 x 10-27 Kg and ^{35}Cl=58.06x1027 Kg.

Solution: Here 2B = 20cm^{-1}, B = 10cm^{-1}

We know,

$$B = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \text{ x } 10^{-34}}{8\pi^2\left(10 \text{ cm}^{-1}\right)(3 \text{ x } 10^{10} \text{ cms}^{-1})}$$

$$\text{But } \ IJ = 1 \text{ Kgm}^2\text{s}^{-2}$$

$$\therefore \ I = \frac{6.626 \text{ x } 10^{-34} \text{ kgm}^2\text{s}^{-2}\text{s}}{8\pi^2\left(10 \text{ cm}^{-1}\right)\left(3 \text{ x } 10^{10} \text{ cms}^{-1}\right)}$$

$$= 2.7973 \text{ x } 10^{-47} \text{ Kgm}^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\left(1.6737 \text{ x } 10^{-27}\right)\left(58.06 \text{ x } 10^{-27}\right)\text{kg}}{\left(1.6737 \text{ x } 10^{-27} + 58.06 \text{ x } 10^{-27}\right) \text{ kg}}$$

$$\mu = \frac{1.6737 \text{ x } 58.06 \text{ x } 10^{-54}\text{kg}}{59.733 \text{ x } 10^{-27} \text{ kg}}$$

$$\mu = 1.6261 \text{ x } 10^{-27}\text{kg}$$

$$I = \mu r^2$$

Or,

$$r = \sqrt{\frac{I}{r}} = \sqrt{\frac{2.7973 \text{ x } 10^{-47} \text{ Kgm}^2}{1.6261 \text{ x } 10^{-27}\text{kg}}}$$

$$= \ 1.3115 \text{ x } 10^{-10} \text{ m} = 131.15 \text{ pm}$$

Example 2: What is the frequency of the rotational line shown by a diatomic molecule, having the moment of inertia value 16.5 x 10^{-40} gcm^2, the excited molecule being in the quantum state J=2?

Solution: Selection rule for rotational transition is $\Delta J = \pm 1$. Since J for excited state = 2, transition occurred from J=1 to J=2

In J = 1, state energy $E_1 = Bh.1(1 + 1) = 2Bh$; $\left[B = \frac{h}{8\pi^2 I}\right]$

and In J = 2, state energy $E_2 = Bh.2(2 + 1) = 6Bh$

So, energy absorbed = $4Bh = h\vartheta$

So frequency absorbed = $4B = \frac{4h}{8\pi^2 I}$

$$\vartheta = \frac{4 \text{ x } 6.625 \text{ x } 10^{-27}}{8 \text{ x } (3.14)^2 \text{ x } 16.5 \text{ x } 10^{-40}} = 2.036 \text{ x } 10^{11} \text{ sec}^{-1}$$

and in wave number $\bar{\nu} = {}^{V}/_{c} = 6.57 \text{ cm}^{-1}$

Example 3: Calculate the moment of inertia of a molecule having isotope combination $C^{12}O^{16}$ given $r_{co} = 1.13$ Å.

Solution: Reduced mass of $C^{12}O^{16} = \frac{12 \text{ x } 16}{12 + 16} \text{ x } 1.66 \text{ x } 10^{-24}$g

$$= 1.14 \text{ x } 10^{-23}\text{g}$$

So, $I = 1.14 \text{ x } 10^{-23} \text{ x } (1.13 \text{ x } 10^{-8})^2 \text{gcm}^2$

Or, $I = 1.146 \text{ x } 10^{-39} \text{ gcm}^2$

Numerical:

Example 1: Calculate the force constants for the bond in HCl from the fact that the fundamental vibration frequency is 8.667 x 10^{-37} Kg?

Solution:

$$\text{m1 (for H atom)} = \frac{1.008}{6.022 \times 10^{23}}\ \text{g} = 1.6739 \times 10^{-27}\ \text{Kg}$$

$$\text{m1 (for H atom)} = \frac{3.55}{6.022 \times 10^{23}}\ \text{g} = 5.8951 \times 10^{-26}\ \text{Kg}$$

$$\therefore \text{ Reduced mass } \mu = \frac{m_1 \times m_2}{m_1 + m_2} = 1.6277 \times 10^{-27}\ \text{Kg}$$

Also it is given that

$$\nu = 8.667 \times 10^{13}\ \text{s}^{-1}$$

$$\therefore\ k = 4\pi^2\nu^2\mu$$

$$= 4 \times \frac{22}{7} \times (8.667 \times 10^{13})^2 \times (1.6277 \times 10^{-27}\ \text{Kg})$$

$$= 483.1\ \text{Nm}^{-1}$$

Example 2: In the near IR spectrum of CO there is an intensive bond at 2144 cm^{-1} . Calculate:

1. The fundamental vibration frequency of CO.
2. The period of vibration,
3. The force constant,
4. The zero point energy in cal/mole.

Solution:

(a) $\bar{\nu} = \frac{\nu}{c}$ or $\nu = c\bar{\nu}$

So frequency (fundamental) of absorption $= 3 \times 10^{10} \times 2144$

$$= 6.43 \times 10^{13}\ \text{s}^{-1}$$

(b) If 6.43×10^{13} vibration occur/sec, then period of vibration i.e, time for one vibration

$$= \frac{1}{6.43 \times 10^{13}} = 1.55 \times 10^{-14} \text{ s}$$

(c) If force constant = k then fundamental frequency

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{12 \times 16}{12 + 16} \times 1.66 \times 10^{-24} \text{ g}$$

$$= 11.38 \times 10^{-24} \text{ g}$$

$$6.43 \times 10^{13} = \frac{1}{2 \times 3.14} \sqrt{\frac{k}{11.38 \times 10^{-24} \text{ g}}}$$

Or, $k = 1.855 \times 10^{6}$ dyne cm^{-1}

(d) Zero point energy = $N\frac{1}{2}$ hν/mole

$$= \frac{1}{2} \times 6.023 \times 10^{23} \times 6.62 \times 10^{-27} \times 6.43 \times 10^{13} \text{ ergs/mole}$$

$$= 1.282 \times 10^{11} \text{ ergs}$$

$$= 3052 \text{ cal}$$

UNIT 5: NUCLEAR CHEMISTRY

5.1 Introduction

First of all radioactivity was discovered by Henri Becquerel. Later it was found that this property is exhibited by not only which blend but why many other salts. Further, it was also found that it the Becquerel rays in fact consist of three types of radiation; alpha beta and gamma. The milestone in the development of nuclear chemistry. Now, different types of nuclear reactions like nuclear fusion fission spallation reactions are expressed Bethe notations. For nuclear radiation released different units like Red, Grey, Rontgen, Rem etc.nuclear fusion or fission release tremendous amount of energy. The energy released by nuclear fission process is used in various types of nuclear reactors. The energy released in nuclear fusion is a basis of radiant energy. However, this process is not yet carried out under controlled conditions.

Objectives:

After studying this unit you should be able to:

- Express various types of nuclear reaction by Bethe notations.
- Explain the difference between nuclear reactions and chemical reactions.
- Explain the Curie theory involved in nuclear reaction.
- Understand the concept of compound nucleus.
- Calculate the energy released in fashion of 1 gram of radioactive substance.
- Know about various types of nuclear reactors.
- Explain the idea about radiolysis.
- Explain about radiation dosimetry.

5.2 Bethe's Notation ANR

A nuclear reaction is represented by an equation indicating the nuclear characteristics of the reactant and the resultants, as

$$^{A_1}_{Z_1}X + {}^{A_2}_{Z_2}a \longrightarrow {}^{A_3}_{Z_3}b + {}^{A_4}_{Z_4}y$$

Where X is the target nucleus, a is the projectile hitting the target, b the particle ejected and y the product or recoil. The same reaction is represented concisely and more elegantly on Bethe's notation.

$$^{A1}X(a,b)^{A4}y$$

It means a general nucleus reaction a+x → y+b is now represented in 1 compact notation as x(a,b)y where x is the target, a is the projectile, y is the resulting nucleus and b is the outgoing particle.

5.3 Types of nuclear reactions (n, p, α, β and γ)

Nuclear reactions may broadly be divided into two types:

a. **Natural radioactivity:**

The spontaneous and automatic emission of radiations such as α, β and γ etc, by the nuclei of certain heavy elements is called natural radioactivity e.g,

i. $_{88}Ra^{226} \xrightarrow{\alpha\text{-emission}} {}_{86}Rn^{222} + {}_{2}He^{4}$

ii. $_{82}Pb^{214} \xrightarrow{\beta\text{-emission}} {}_{83}Bi^{214} + {}_{-1}e^{0}$

b. Artificial radioactivity:

When a stable element is rendered Radioactive by bombardments with alpha beta gamma etc. the phenomena is called 'artificial' or 'induced radioactivity'. The new radioactive elements or isotopes so produced disintegrate exactly in the same manner as the natural radioactive elements, e.g., U^{235} gives a tremendous amount of energy but it is difficult to get U^{235} as natural uranium contains only 0.72% of U^{235}. $_{94}Pu^{239}$ does not occur in nature but can be made from more abundant U^{233} (99.3%) undergoes fission readily like $_{92}U^{235}$ and is prepared from U^{238} as follows:

$$\begin{tikzcd}
{}_{82}U^{238} + {}_{0}n^{1} \arrow[r] & {}_{92}U^{239} \arrow[r, "\beta\text{-emission}"] & {}_{93}Np^{239} + {}_{-1}e^{0} \arrow[d] \\
& & {}_{94}Pu^{239} + {}_{-1}e^{0}
\end{tikzcd}$$

In this nuclear reaction, U^{238} is bombarded by fast moving neutrons and β-particles are given out. Such nuclear reaction is called (n, β) reaction. U^{238} is a non-radioactive element but becomes radioactive when bombarded with neutrons due to the formation of U^{239} which is a β-emitter. Therefore U^{239} is called as an artificial radioactive element.

5.4 Nuclear reactions

We know that in a chemical reaction, only electrons (extra nuclear part) of the atom participate, while the nucleus of the atom remains unaffected. However, the reverse reactions i.e., where only nuclei of atoms take part in reactions) are also possible. Such reactions in which the nucleus of an atom itself undergoes spontaneous change or interact with other nuclei of lighter particles resulting new nuclei and one or more lighter particles are called nuclear reactions.

Important features of nuclear reactions:

1. Nuclear reactions are written like a chemical reaction. As a chemical reaction, reactants in a nuclear reaction are written on the left hand side and products on the right hand side with an arrow in between them.
2. Mass number and atomic number of the element are written in a nuclear reaction. Mass number and atomic number of the element involved in a nuclear reaction are inserted as superscript and subscript, respectively on the symbol of the element. For example ${}_{17}Cl^{35}$, ${}^{37}_{17}Cl$ or Cl^{35}_{17} stands for an atom of chlorine with mass number 35 and atomic number 17.
3. Mass number and atomic number are conserved. In a nuclear reaction, the total mass numbers and total atomic number are equal on both the sides of reaction.
4. Energy involved in nuclear reaction is indicated in the product as -Q or +Q for reactions accompanied by absorption for release of energy, respectively.
5. Important projectiles and their symbol are α-particles (${}_{2}He^{1}$), proton (${}_{1}H^{1}$ or p), deuteron (${}_{1}H^{2}$ or ${}_{1}D^{2}$), neutron (${}_{1}n^{0}$), electron (β-particle, ${}_{-1}e^{0}$ or e) and positron (${}_{+1}e^{0}$).

$${}_{5}B^{11} + {}_{1}H^{1} \longrightarrow {}_{6}C^{11} + {}_{0}n^{1} + Q$$

A shorthand notation can also be used for the above nuclear reaction, as shown below:

$${}_{5}B^{11}(P,n) \longrightarrow {}_{6}C^{11}$$

Difference between nuclear reactions and chemical reactions:

Nuclear reactions differ from chemical reactions as follows:

1. In chemical reactions, rearrangement of outermost electrons of the reacting atoms occurs, while the nuclei remain unaffected. Thus, the element remains the same during the course of electrons. On the contrary, in the nuclear reactions, new nuclei and so new elements are formed during the course of the reaction.
2. The chemical reactivity of the element is dependent on the nature of the bond present in the compound. However, the nuclear activity of the element is independent of its state of chemical combination, e.g., for Thorium whether present as such or in the form of its compound will always show radioactivity.
3. The amount of energy released in the nuclear reactions is million times greater than that produced in chemical reactions. This occurs due to a small loss of mass in nuclear reactions.

4. A chemical reaction is balanced in terms of mass only, while a nuclear reaction is balanced in terms of both mass and energy.
5. The rate of a chemical reaction depends on temperature, pressure and Catalyst. However, the rate of nuclear reaction has no effect of external conditions.
6. A chemical reaction can be reversed under suitable conditions, whereas a nuclear reaction cannot be reversed.

5.5 Conservation of quantities (mass energy and linear momentum) in nuclear reactions

Conservation of nuclear momentum:

The initial momentum of the incident projectile (mass M and velocity v) equals that of the resulting compound nucleus (X + a) of mass (M + m) and velocity ν

$$m\nu = (m+M)V \qquad \ldots\ldots\ldots(1)$$

Hence,

$$V = \left(\frac{m}{m+M}\right)\nu \qquad \ldots\ldots\ldots(2)$$

Since, the compound nucleus of mass (M + m) is set in motion with velocity v, the kinetic energy of the compound nucleus

$$T_{cn} = \frac{1}{2}(m+M)\nu^2$$

$$= \frac{1}{2}(m+M)\frac{m^2}{(m+M)^2}\nu^2$$

$$= \frac{1}{2}m\nu^2\frac{m}{m+M}$$

$$= T_a.\frac{m}{(m+M)} \qquad \ldots\ldots\ldots(3)$$

Where T_a is the kinetic energy of the projectile.

Energy on Laboratory and centre of mass systems:

Since, a fraction m/(m + M) of the T_a is used in providing translational energy of the compound nucleus, the fraction of T_a available for affecting the nuclear reaction is $1 - \frac{m}{m+M} = \frac{M}{m+M}$ of T_a

The component $\frac{M}{m+M}T_a$ available for affecting the nuclear reaction is known as kinetic energy of the projectile and the target on the Centre of Mass System (CMS). Thus we summarise kinetic energy of projectile on Laboratory System (LS) $T_a = \frac{1}{2}mv^2$, but on CMS it is M/m+M is used up providing translatory motion to a compound nucleus.

Conservation of angular momentum:

The total angular momentum that the projectile brings to the reacting system = I = (I+S) where I and S are the orbital and spin angular momenta of the projectile. This I together with I’, the total angular momentum of the target stays conserved after the nuclear reaction i.e.

$$I+I' = \sum (I_1+I_2 + \ldots.)$$

Where i_1, i_2 ...are the total angular momentum of product species 1, 2, 3….. of the nuclear reaction.

The on the theory of Blatt and Weisskopf the plane wave associated with the incident particles is resolvable into a set of partial waves, corresponding to a series of I values

$$1 = 0 \text{ (s wave) with } r = \lambda$$

$$\lambda = 1 \text{ (p wave) with } r = 2\lambda$$

$$1 = 2 \text{ (d wave) with } r = 3\lambda$$

Each particle waves transfer the different amount of angular momentum to the target nucleus

Conversion of energy:

In a reaction X + a → b + Y the sum of the rest mass energies of the particles and their Kinetic energies must be conserved, thus

$$(m_x + m_a)931 + E_a = (m_y+m_b)931 + E_b + E_y \qquad \text{......(4)}$$

Where, the MS are the rest masses and E_s are the kinetic energy. X the target is assumed to be initially at rest with zero kinetic energy.

Rearranging equation (4)

$$[m_x + m_a - m_b + m_y]931 = E_b + E_y - E_a = Q \qquad \text{......(5)}$$

Where Q is the energy of the reaction.

$$Q = 931\Delta m \qquad \text{......(6)}$$

Δm being the net mass loss.

5.6 Nuclear cross section

A very important quantity in nuclear reaction is the reaction cross section. This has the dimension of area and is shown by σ_i in units of barn*, the subscript i indicates the particular reaction, σ_i represents the number of reactions of the type shown by i that takes place per cm^2 per second under conditions of unit density of target nuclei and unit flux of the incident particles. In other words, the cross section σ_i is a measure of the probability of reaction i occurring, or its yield under the above set of conditions. For each reaction cross section has to be experimentally determined from the measured reactions yield and known surface density of target nuclei (N_o cm^{-2}) and the projectile flux (φ cm^{-2} s^{-2}).

Cross section and reaction rate:

Consider a thin sheet of target containing N_o (spherical) nuclei per unit.

$$\rightarrow \sigma(\text{in } cm^2) = \frac{\text{Collision } cm^{-2}\, s^{-1}}{\varphi\ cm^{-2}s^{-1}\ N_o\ cm^{-2}}$$

*N_o ($=10^{-33}m^3$) cm^{-2}, thus 1 b = 10^{-24} cm^2 area, and a beam of projectiles considered to be points passing through the sheet normally. Let the beam consists of n particles per cm^3 all traveling with a velocity v cms^{-1}. The collision rate between the projectiles and the target nuclei would be given by:

$$\text{Collision rate } \alpha \text{ nv } N_o = \sigma\varphi N_o\ cm^{-2}\ s^{-1}$$

Where α is the reaction cross section. It follows that:

The geometric and reaction cross section:

The geometric cross section of a spherical nucleus is simply πR^2, where R is its radius given by 1.4 x $A^{1/3}$ F, where A is the mass number. Obviously, for isotopic nuclides and nuclides of close by elements R varies but very slightly. The nuclear radius just double from 4.2F for ^{27}Al to 8.4F for ^{216}Po. This corresponds to Geometric cross section of 0.554 and 2.217b for the two nuclei. The reaction cross section is almost always related to the geometric cross-section which varies but slightly amongst nuclides. On the other hand, the reactions cross section varies vary widely from 10^{-3} 10^{6} b amongst reactions[5]. The σ varies from reaction to reaction between the same pair of reactants, and for the same reaction often with the energy of particles. It is therefore necessary to indicate the specific reaction by a subscript as σ_s for neutron induced fission, or as σ(d,p), σ (d,n), σ (d,y) for the specific reaction. Usually, σ_i stands for the total of all processes between the two reactants. For instance, thermal neutrons interact in two ways with $\sigma_f = 531$ b which means in a total of 584 interactions only 53 on 9% area of (n, r),(d, n),(d, 3n), and (d, p). The total cross section σ_i is 2b. Total target area is interpreted as being divided into areas σ (d, y), σ (d, n).... The area σ_i assigned to the ith reaction is a measure of the probability of that reaction occurring. Thus, in the previous example given σ_t=2b and σ(d, y) = 1mn, it means that out of 2000 deuterons striking the ^{232}Th target only one will be captured radioactively.

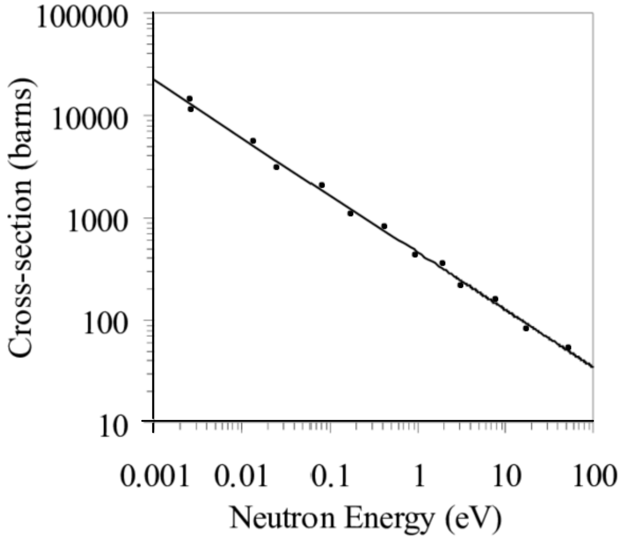
A few values of thermal neutron capture or specific reaction cross-sections are given below to show the range of variation of reaction cross-sections. The cross-section for xenon isotope shows the effect of the magic number of 82 of neutrons.

$$\left.\begin{array}{ll} {}^{6}Li_{(n,\,\sigma)};\ \sigma = 940b; & {}^{134}_{54}Xe_{30};\ \sigma_c = 0.25b; \\ {}^{6}Li;\ \sigma_t = 0.037b; & {}^{135}Xe_{31};\ \sigma_c = 0.16b; \\ {}^{6}Li;\ \sigma_a = 19910b; & {}^{136}Xe_{32};\ \sigma_c = 0.16b; \end{array}\right\}$$

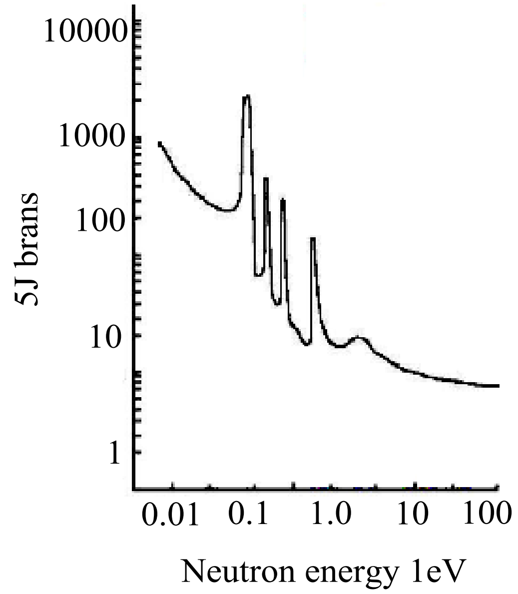
Variation of neutron capture cross section with energy:

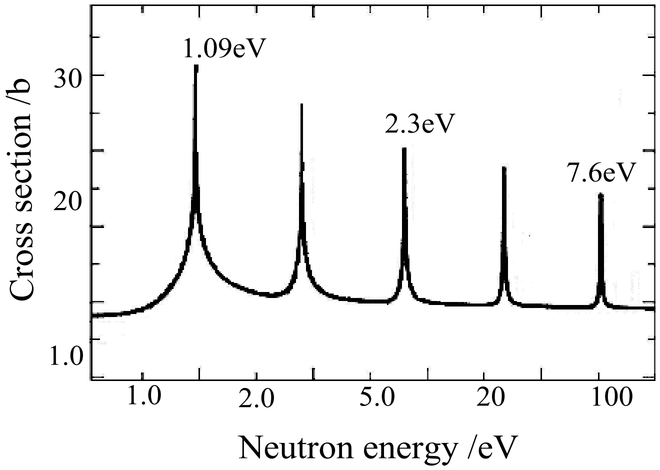
The 1/N law:

Generally, the slow neutron capture cross section varies inversely as the neutron velocity, which is referred to as the 1/v law. In other words, σ varies inversely as the square root of the Newton energy. Fig 1 (a) shows this variation for the ^{10}B (n, α) ^{7}Li reaction. Hence long σ is plotted against log neutron energy. In many cases, beyond a limit, the curve for the 1/v law gets superimposed by sharp peaks at definite values of neutron energy. Fig 1 (b) and (c) show this effect for the (n, r) reactions in silver and zirconium respectively. This peak absorption are referred to as a resonance captures, considered in the next section.


100000
10000
1000
100
10
Cross-section (barns)
0.001
0.01
0.1
1
10
100
Neutron Energy (eV)

(a)


10000
1000
100
10
1
5J brans
0.01
0.1
1.0
10
100
Neutron energy 1eV


1.09eV
2.3eV
7.6eV
30
20
1.0
Cross section /b
1.0
2.0
5.0
20
100
Neutron energy /eV

(b) **(c)**

Fig.1. Variation of neutron cross section with energy: the 1/v law (a) $^{10}B_{(n,\ \alpha)}\ ^{7}Li$ reaction for ^{4a}(b) $^{109}Ag_{(n,\ r)}\ ^{110}Ag$ reaction[6]. In the latter case, the 1/v law up to 1 eV is followed by resonance captures. (c) Neutron resonance capture in zirconium[7].

a. Introductory Nuclear Physics, by D. Halliday[4a], © 1950, 1955, John Wiley and Sons, Inc. reproduced with permission.
b. Nuclear and radiochemistry by G. Friedlander, J.W Kennedy and J.M Miller, (c) 1964. John Wiley and sons, reproduced with permission.
c. WH Havens, C S Wu, LJ rainwater and CL Meaker 7, reproduced permission of the Columbia University.

The de Broglie wavelength of slow neutron of energy 1 eV is 2.86 $\times 10^{-11}$m, which is many times greater than the dimensions of the target nucleus. The de Broglie wavelength of a particle is given by $\lambda = h/p = h/\sqrt{2mE}$ where m is its mass and E is energy. Substituting E =1eV = 1.6×10^{-10}J and values of other constants,

$$\underset{(1\text{eV neutron})}{\lambda} = \frac{6.6262 \times 10^{-34}}{(2 \times 1.009 \times 1.66 \times 10^{-27} \times 16 \times 10^{-19})^{1/2}}\ \text{m}$$

$$= 2.86 \times 10^{-11}\ \text{m}$$

For an increase of neutron energy by a factor of 10^2, the wavelength decreases by a factor of 10. Thus, λ (1 Me V neutron) = 2.86×10^{-14}m, which approaches the nuclear dimension.

This means a neutron wave of 1eV of energy surrounds a very large number of target nuclei, hence has a great capture cross-section. As the neutron energy increases, the wavelength diminishes and the number of nuclei and compass buy it falls rapidly and hence the decrease of σ as per 1/v law[8].

5.7 Compound Nucleus Theory

Based on the liquid drop model of the atomic nucleus, Bohr proposed the theory of nuclear reactions in 1936 which envisages the formation of a compound nucleus between the target nucleus and the projectile. The basic concepts of this theory are presented below.

The concept of the compound nucleus:

a. Under favorable conditions, the projectile particle and the target nucleus fuse together to form a compound nucleus C*.

Thus,

$$ {}^{A_1}_{Z_1}X + a\,{}^{A_2}_{Z_2} \longrightarrow {}^{A_1+A_2}_{Z_1+Z_2}C^* $$

e.g

$$ {}^{24}\mathrm{Mg} + d \longrightarrow {}^{26}\mathrm{Al}^* $$

$$ {}^{60}\mathrm{Ni} + \alpha \longrightarrow {}^{64}\mathrm{Zn}^* $$

$$ {}^{63}\mathrm{Cu} + p \longrightarrow {}^{64}\mathrm{Zn}^* $$

This last shows how the same compound nucleus may be formed from two (or more) sets of reactants.

b. The compound nucleus would be in the excited state, it the excitation energy being the sum of the binding energy e of the projectile particle in the compound nucleus and the kinetic energy of the projectile particle in the compound nucleus and the kinetic energy of the projectile on CMS (sec.5.3.2)

c. The excess of excitation energy brough in by the incoming particle will be very quickly shared by the nucleons of the compound nucleus in a random way. The time (t) for this is just the time needed for the particle (of velocity n) to traverse a diameter (2R) of the target nucleus.

$$ T \cong 2R/V $$

Thus, with fast neutrons of energy 1 MeV, the velocity is $\sim 10^{7}$ ms^{-1} and taking the nuclear diameter to be with $\sim 10^{-14}$ m, the time for energy randomization is $\sim 10^{-21}$ s. With slow neutrons of $V \sim 10^{3}$ ms^{-1}. t is about 10^{-17} s. This is referred to as the natural nuclear time. The excess energy distribution is a random process. This means that the distribution is such that it keeps varying with time in such a way that at some moment one set of nucleus, come of the Fermi gap (~8 MeV per nucleon), that nucleon or group of nucleus succeed in separating from the compound nucleus, resulting in a nuclear reaction of a certain type.

d. Thus the overall nuclear reaction x(a,b)Y is a two step process, viz. the formation of the compound nucleus and its subsequent DK to give products. the occurrence of the second stage of the nuclear reaction of one kind or another referred to above is a relatively a slower process, involving times of the order of 10^{-15}, 10^{-14} s, compared to the natural nuclear time (10^{-17} -10^{-21} s). This means the compound nucleus has a relatively long life.

This concept has significant implications:

i. The same compound nucleus may be formed in more than one way, i.e. from different sets of target and projectile pairs.

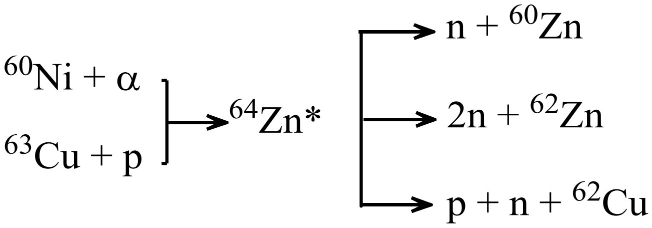
ii. Because of its long life the compound nucleus forgets its parentage, i.e. how it was formed.

iii. The subsequent decay of the compound nucleus is independent of the mode its earlier formation, and the decay may occur also in more than one way, the relatively yields depending on the energy of excitation.

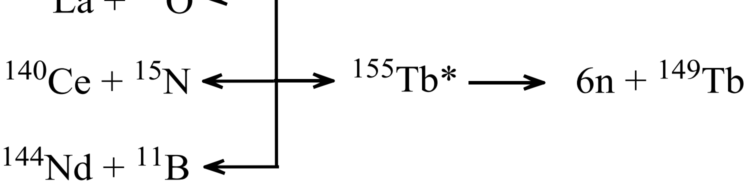
iv. Being an independent process, the products of the decay of the compound nucleus, may be admitted isotropically (i.e. nearly uniformly in all directions), without relation to the direction of the incident particle.

The following reaction studied by SN Ghoshal makes these points clear[9].

Target + projectile → compound nucleus → decay products



As for the examples, we have the reaction studied by Alexander and Simonoff[10].



And the reactions, studied by the French group at Saclay:

$$\begin{tikzcd}
{}^{59}\mathrm{Co} + {}^{20}\mathrm{Ne} & & \\
 & {}^{79}\mathrm{Rb}^{*} \arrow[ul] \arrow[dl] \arrow[r] & p + {}^{79}\mathrm{Kr} \\
{}^{63}\mathrm{Cu} + {}^{16}\mathrm{O} & &
\end{tikzcd}$$

The excitation states of the compound nucleus:

a. The energy of excitation: the total energy of excitation of a compound nucleus is the result of two contributions.

   i. The kinetic energy of the projectile on the CMS and

   ii. The bonding energy of a particle on the compound nucleus. The following example illustrates the calculation. the reaction is the bombardments of magnesium by 8 MeV deuterons, the compound nucleus formed being ^{26}Al* whose excitation energy is the sum of two terms:

      1. The kinetic energy of the deuteron in striking ^{24}Mg nuclei on CMS: viz (fig) Eq.1) = (24/26)x8 = 7.38 MeV and
      2. The binding energy of the deuteron in the ^{26}Al is given by:

$$[m(^{24}Mg) + m(^{2}D) - mm(^{26}Al)]931 =$$

$$23.985045 + 2.104102) - 25.986900]931$$

$$= 0.012247 \times 931$$

$$= 11.40 \text{ MeV}$$

Hence, the energy of excitation of

$$^{26}Al^{*} = 7.38 + 11.40 = 18.78 \text{ MeV}$$

b. Distribution of the excitation energy:

As mentioned earlier the total excitation energy is distributed randomly between the nucleuses of the compound nucleus. The probability of a uniform distribution is the lowest. For instance, in the (Mg^{+2}D) the reaction described above, if the excitation energy of 18.78 MeV were to be uniformly distributed over the 26 nucleons of the compound nucleus, each new would get about 0.72 MeV which is too low to affect any nucleon emission. In such a case, the nuclear reactor citation can occur only by emitting radiation.

A large excitation energy of several MeV results in many nuclei being raised to energy levels much higher than their ground state, besides the presence of considerable rotational and vibrational energy. The distribution of this energy among the nucleus is random, implying a continuous variation, as a result of incessant interactions amongst them (possible on the Liquid Drop or the gas model). The excess energy may be concentrated on a given group of nucleons at one incident and on another group at another instant. Each distribution corresponds to the filling of certain energy level which varies from moment to moment. Such a distribution is a quasi stationary or a chaotic state. It will be a large number of closely spaced energy levels the widths of which are greater than the energy separation between the levels. In other words, these levels overlap and no discrete energy level characteristic of single well defined quantum state can be distinguished: it is practically a Continuum. While the total energy and angular momentum remain constant, there maybe a vast number of ways of distributing this amongst the nucleons of the compound nucleus and the latter keeps oscillating between the configurations. Such a system can be treated statistically on the Fermi gas model of the nucleus. In A nucleus like 63 CU excited to 25 MeV, the density of energy level is as high as 500 per MeV per, corresponding to a mean separation of 2 of KeV between two adjacent level.*

This high-energy closed spaced levels constitute the virtual levels as a distinct form well separation discrete levels lying below the top of the nuclear well and referred to as the bound levels (Fig. 2) De-excitation from the ground level results in Photon emission,

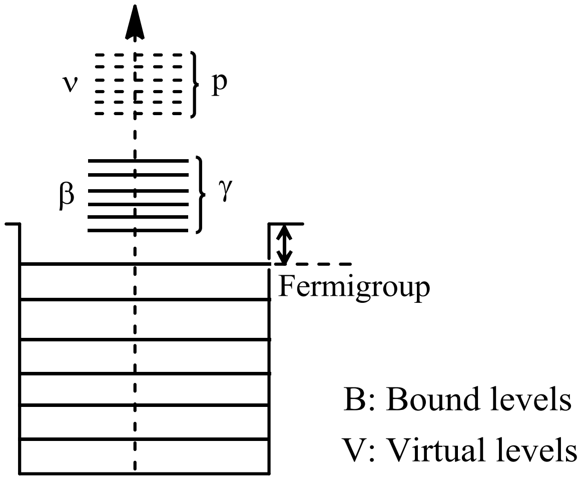


Fig.2 Nuclear excitation

While de-excitation from the virtual levels happened by the admission of a particle, as an n or p, or a group of particles as 2n, d, α, often accompanied by r. For the particle omission to occur, the particular nucleon, or a small group of nucleons, should receive the necessary energy (i.e. the Separation energy of about 8 MeV per nucleon + Coulomb* and other barrier energies involved), concentrated by chance on the group during the random and incessant redistribution. This cannot be very frequent. However, once such a favored configuration is reached, the nucleon emission follows without delay (energy being > separation energy), rather similar to the process of ionization of an atom once the atom is excited about the ionization potential.

Under low excitation (energy < separation energy) photon emission is the dominant mode of de-excitation.

De-excitation of the compound nucleus:

Life times and line widths :

Every excitation level has some line width (Γ), measured at half height (Fig.2), which varies from about 0.1 to about 10^4 eV ,depending on the energy of excitation and the mass number of the nucleus. Also each excited state has a mean life time (T= 1/ decay constant). By the principle of uncertainty, the product of the uncertainty is of the two is H, thus for level i,

$$\Delta\Gamma_i \, \Delta T = h = 1.0544 \times 10^{-34} \text{ JA}$$

The mean lifetime is given by-

$$T = \frac{h}{\Gamma} = \frac{6.6 \times 10^{-16}}{\Gamma} \text{ s}$$

Where Γ is in eV. As Γ varies from 0.1 to 10^4 eV, T varies from 10^{-15} to 10^{-15} to 10^{-20}s. Since each mode of decay has a different line width,

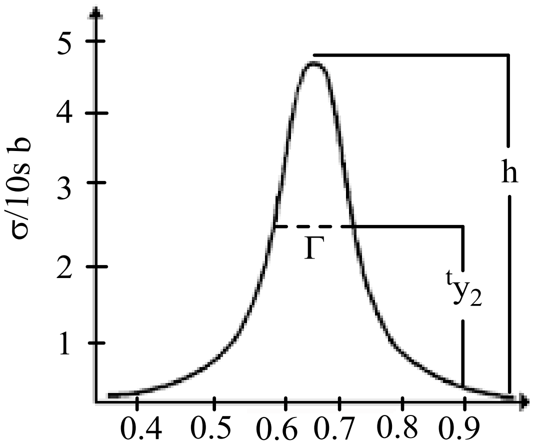


Fig.3 -Resonance capture of 0.65 eV neutrons by radium showing the line width Γ.

$$\Gamma_{total} = \Gamma_4 + \Gamma_n + \Gamma_{2n} + \Gamma_p + \Gamma_a \ldots\ldots$$

Where Γ_y, Γ_n ... are line width for individual modes of decay, as radiation or photon width Γ_y, neutron width Γ_n etc. Each term is a measure of the probability of emission per second for the particle indicated by the subscript.

5.8 Nuclear fission

Hahn and Stressmann (1939) observed that when Uranium-235 is bombarded with slow neutrons, neutron is first of all captured by the uranium nucleus and then it breaks up into two nuclei, i.e, $^{56}Ba_{140}$ and $^{36}Kr_{92}$ of somewhat the same size. The speed of the neutron is reduced by passing them through a moderator, e.g, heavy water or graphite.

$$_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{56}Ba^{140} + {}_{36}Kr^{93} + {}_{30}n^{1} + \text{energy}$$

The phenomenon of splitting up of a nucleus of a heavy atom into two nuclei of somewhat the same size with the liberation of huge amount of energy is known as nuclear fusion.

The secondary neutrons, which are produced, strike other uranium atoms, thus causing more fission along with release of more neutrons and more energy. Thus, this process continues in the form of a chain reaction and ultimately and explosion results on account of tremendous amounts of energy. This is the principle of atom bomb.

Mechanism of nuclear fission:

The phenomenon of nuclear fission has been explained by liquid drop model. The atomic nucleus has many similarities to a liquid drop. A liquid drop is spherical in shape due to surface tension. If sufficient energy is supplied to overcome the forces of surface tension, the liquid drop may be forced to change its shape from a sphere to an ellipse then to a dumbbell and ultimately into two spheres. Similarly, efficient energy is applied on the uranium nucleus through the neutron bombardment, then the compound nucleus, similar to liquid drop, main break into two nuclei of comparable sizes.

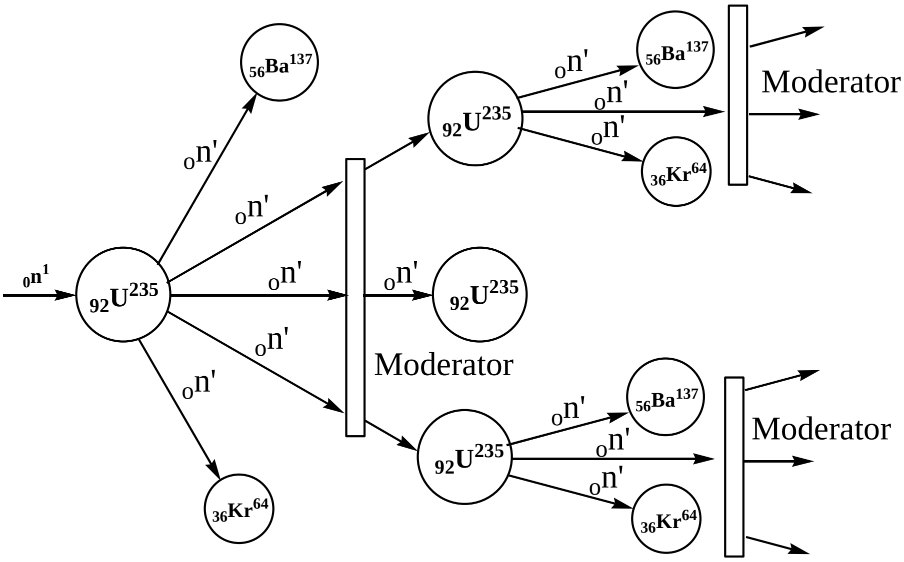


Fig.1 Chain reaction in nuclear fission

The mass loss can be estimated as follows:

Mass of reacting particles:

$$_{92}U^{235} = 235.11750 \text{ amu}$$

$$_0n^1 = 1.00898 \text{ amu}$$

$$= 236.12648 \text{ amu}$$

Mass of product particles

$$_{56}Ba^{140} = 139.5770 \text{ amu}$$

$$_{36}Kr^{93} = 92.92640 \text{ amu}$$

$$_0n^1 = 3.02694 \text{ amu}$$

$$= 235.91104 \text{ amu}$$

So, loss of mass = (236.12648-235.91104)amu

= 0.21544 amu

The energy released per nucleus of U^{235} undergoing fission is given as follows.

Energy released (per U^{235} nucleus) = 0.21544 x 93.5 MeV

= 200.5 MeV

Energy released per mole of U^{235} nucleus = (6.023 x 10^{23} x 200.5) MeV

$\therefore$ Energy released per 235 gram of U^{235}= 1.2076 x 10^{26} MeV

Energy released per gram of $U^{235} = \frac{1.2076 \text{ x } 10^{26}}{235}$ MeV

$= 5.1387 \times 10^{23}$ MeV

$= 5.1387 \times 10^{23} \times 1.6021 \times 10^{-16}$ KJ

$= 8.233 \times 10^{7}$ KJ

($\therefore$ 1MeV = 1.6021×10^{-13} J = 1.6021×10^{-16} KJ)

This energy can be compared with the energy of 2 kJ obtained from complete combustion of 1 g of coal.

The importance of fission:

It was on January 9, 1939 in that Otto Hahn and Strassmann of Germany announced the discovery of nuclear fission, whereby uranium nucleus capturing a neutron splits into two fragments of comparable mass, as ^{140}Ba and ^{94}Kr (or similar other pair) involving sizeable mass loss and the release of equivalent amount of energy besides 2-3 free neutron. Coming just eight month before the outbreak of World War 2, the discovery was destined to play a spectacular role in bringing to a dramatic and the 6 year old war in a matter of days, in August 1945. The twin old war features of nuclear fission which leads to such an outstanding result where the release of a fantastic amount of energy of the order of 200 MeV per fission and the simultaneous liberation of 2-3 free neutrons. The last, if properly harnessed could sustain long Chains of fission providing the key to limitless energy.

The process of fusion:

When fission nucleus (^{232}Th, ^{235}U, ^{238}U, ^{239}Pu) capture a neutron, it gets excited and distorted in shape under the action of two opposing forces (i) the coulomb force of repulsion causing the shape distortion, and (ii) the force of surface tension tending to restore the initial near symmetrical shape. Under conditions when the former dominates, the deformation keeps increasing till a point of no return is reached when the parent nucleus fissions into two fragments F_1 and F_2 corresponding to a pair of nuclei for or down in the middle part of the periodic table as Kr and Ba or Sc and Xe or Zr and Te and so on.

In the process significant mass loss occur (~0.2u, equivalent energy = $\Delta m \times 931 \approx$ 200 MeV) and 2-3 free neutrons are shed.

$$^{235}\text{U} + \text{n} \longrightarrow {}^{236}\text{U}^* \longrightarrow {}^{95}\text{Sr} + {}^{139}\text{Xe} + 2\text{n};\ \Delta m = -0.2\text{u}$$

$$(\approx 200 \text{ MeV})$$

Fission products:

Even so the primary products of fission, (F1 and F2) contain excess neutrons compared to stable isotopes of their mass number. The primary fission product decay by β-emission and continue to do so with increasing half lives till the stable product is reached isobaric with the primary fragment, as shown below:

$$\begin{tikzcd}
& {}^{99}\mathrm{Nb}_{41} \arrow[r, "\beta^-", "2.6\mathrm{min}"'] & {}_{42}\mathrm{Mo} \arrow[r, "\beta", "66\mathrm{h}"'] & {}_{43}\mathrm{Tc} \arrow[r, "\beta^-", "2.1\mathrm{x}10^5\,\mathrm{y}"'] & {}_{44}\mathrm{Ru}\ \text{(Stable)} \\
{}^{236}\mathrm{U}^* \arrow[ur] \arrow[dr] & & & & & \\
& {}^{133}_{51}\mathrm{Sb} \arrow[r, "\beta^-", "2.3\mathrm{min}"'] & {}_{52}\mathrm{Te} \arrow[r, "\beta", "1.2\ \mathrm{min}"'] & {}_{53}\mathrm{I} \arrow[r, "\beta^-", "20.8\mathrm{h}"'] & {}_{54}\mathrm{Xe} \arrow[r, "\beta^-", "5.29\mathrm{d}"'] & {}_{55}\mathrm{Cs}\ \text{(Stable)}
\end{tikzcd}$$

Fragments:

Fission products: Mass Distribution:

The mass distribution between the two primary fragments F_1 and F_2 is generally asymmetrical, the mass number A, of the lighter fragment F_1 ranges from 85 to 105 while the mass number A_2 of the heavier fragment F_2 varies from 150 to130. The probability of a symmetric fission into two fragments of nearly equal mass ($A_1=A_2 \cong 117$) is the lowest, never exceeding 0.05 per cent.

A term frequently employed in describing the mass distribution is the cumulative chain fission yield defined as

$$Y_{(A)} = \frac{\text{Number of product nuclei of mass no.A}}{\text{Total amount of nuclei fissioned}} \text{ x } 100$$

A typical fission fragment yield curve as a function of mass number A.

Fission Fragments: Charge Distribution:

We cannot know directly the charges Z_1 and Z_2 of the initially formed the fission fragments as they are mixed up with a large number of β-decay products. However, since the entire β-decay products are isobaric with the primary formed fragments F_1 and F_2 and their most stable end products of charges and Z_2 of β-decay can be calculated by eq. 3.2.4 (Text) for given A_1 and A_2 values, the charger Z_1 and Z_2 of the initially formed primary fragments are calculated on the theory of equal charge displacement i.e.

$$Z_1 - Z^o{}_2 = Z_1 - Z^o{}_2 \qquad ....(1)$$

and of course $Z_1 + Z_2 + Z_f$ charge of the fissioning nucleus (= 92 in the case of Uranium). This thereby leads to:

$$Z_1{}^0 = \frac{1}{2}(Z_f + Z_1 - Z_2)$$

$$Z_2{}^0 = \frac{1}{2}(Z_f + Z_2 - Z_1)\text{----------}(2)$$

Fission fragments: Energy distribution:

the net mass loss (Delta m) in the fission process, less by kinetic energy of the 2 or 3 neutrons released, is the total kinetic energy of the two fission fragments between these in the inverse ratio of their masses. for atypical distribution of energy between the fission products.

Fission neutrons:

The number of secondary neutrons created in ea 8ch fission determines the number, length and divergence of fission chains. Therefore we need to know the number v of the neutrons emitted per fission. But as well the neutrons captured do not lead to fission, what is relevant is the number of neutrons n emitted per neutron used up. this is given by-

$$\square = \mathrm{v}(1+\alpha)\frac{\square\square\square}{\square\square+\square\square}\dots\dots\dots\dots\dots\dots\dots(3)$$

Where (fig) i.e the ratio of cross sections of Alpha decay of the fission nucleus to that for fission. the n values for or different fissioning nuclei are given below-

Fission nucleus	U(natural)	^{233}U	^{235}U	^{239}Pu
Half-life/y	4.5×10^9	1.6×10^8	7×10^8	2.4×10^4
n	1.36	2.28	1.27	2.08

5.9 Nuclear reactor

A controlled Nuclear Fission reaction: During the nuclear fission the number of neutrons resulting from a single fission is known as the multiplication factor (α). There could be three cases.

1. Where Alpha is less than 1:

   the chain reaction is not possible

2. When Alpha is equal to 1:

   in such cases, the fission of a single nucleus releases only one and neutron. the energy thus would be released in a controlled manner. it would then be possible to put this energy to a particle use and the reactor is said to have become critical under these conditions.

3. When Alpha is greater than 1:
4. in such cases, the number of neutrons released from a single fission exceeds one, and the Rapid multiplying effect of the neutron release would make the release of energy unmanageable. this leads to an explosion. a typical example of this uncontrolled Nuclear Fission is an atomic bomb.

   Thus, it can be understood that if the energy released during fission is to be utilised in a profitable way the number of released neutrons (called secondary neutrons) should be controlled so that the reaction proceeds at an optimum study rate, the equipment used for carrying out the fission reaction in a controlled manner is called a nuclear reactor. reactor consists of (a) a fissionable material (uranium enriched in U^{235} (2-3%) (b) A moderator (graphite or heavy water, D_2O) to slow down the neutrons, thereby increasing the efficiency of their capture to bring about a fission reaction, and (c) control rods made up of barren steel cadmium which capture some of the neutron so that the chain reaction does not become violent by having too many neutrons. the control rods are inserted between the fuel elements and they can be raised aur lowered to control the chain reaction. the large amount of heat energy released in the form of heat is removed by a liquid called coolant. coolant is generally a liquid having very low vapour pressure. the coolant transfers this heat to water in heat exchangers to generate steam. the steam then runs the turbine generator to produce electricity.

   To protect the environment from the gamma rays and neutrons escaping from the reactor, a protective cover is provided. it is made of special concrete of nearly 2.5 metre thickness.

nuclear reactors in India:

1. Apsara reactor (1956):

It is the swimming pool reactor which consists of a lattice of enriched uranium fuel immersed in a very large pool of water, which acts as a moderator, coolant and shield.

2. Circus (1960)

   The name is based on the name of a star close to our solar system. it is a natural Uranium heavy water moderated and light water cooled high flux research reactor and has a terminal power of 40 MW. the standard fuel rod contains about 55 kg of natural Uranium.

3. Zerlina (1961):

   the name stands for zero energy letters investigation nuclear assembly, as it was manufactured to study the lattice assemblies of different kinds. the standard fuel rod contains about 45 kg of natural uranium and heavy water is used as a moderator.

4. Purnima (1972):

   It is the first Indian experiment zero point energy fast reactor. it uses plutonium fuel as a reactor.

5. R-5:

   It is a terminal research reactor with a normal power of 100 MW. it is situated near the Circus reactor.

Nuclear power stations in India:

India has several nuclear power stations at:

1. Narora Atomic Power Station, Narora (U.P)
2. Rajasthan Atomic Power Station, Rana Pratap Sagar, near Kota Rajasthan.
3. Tarapore Atomic Power Station, Tarapore (Maharashtra)
4. Madras Atomic Power Station, Kalpakkam (Tamil Nadu).

5.10 The natural uranium reactor

For controlled release of fission energy, the chain reaction is carried out in a device called a nuclear reactor. the fission is controlled in such a manner that on an average only one neutron is left from each fission to excite further fission. Cadmium rods are used to observe the excess of neutrons. The chain reaction that remains sturdy and within control. the neutrons permitted to cause fission are slowed down by passing through moderators such as graphite and heavy water. most of the fission energy is released in the form of heat. the the fissionable radioactive material thus serves as an excellent fuel. the heat produced is used to derive turbo-generators for production of electricity. nuclear fuels are also used in machine proposition as, for example,in war ships and submarines.

1. Thermal reactors:

In these reactors the neutrons released during the the fashion of 235 u are made to collide with light nuclei so as to lower their speed. such a nucleus is called a moderator. commonly used moderators, as mentioned above, are heavy water and graphite. Most thermal reactors use oxide of ^{235}U as fuel taken in the form of Aluminium plated rods. There is a provision to insert cadmium rods into the reactor in case the rate of the fission reaction becomes very high.

The heat generated in the reactor is removed by circulating a liquid called coolant around the reactor. The coolant is generally and alloy of sodium and potassium. the coolant pipes are lead to heat exchanger where they are immersed in water which gets converted into steam by the heat of the coolant. The steam is used to run the turbine for the generator of electricity.

A sufficiently thick spherical concrete structure is built around the reactor to protect the workers from the damaging effect of Gamma radiations.

A diagrammatic sketch of the plant is shown in Fig.1

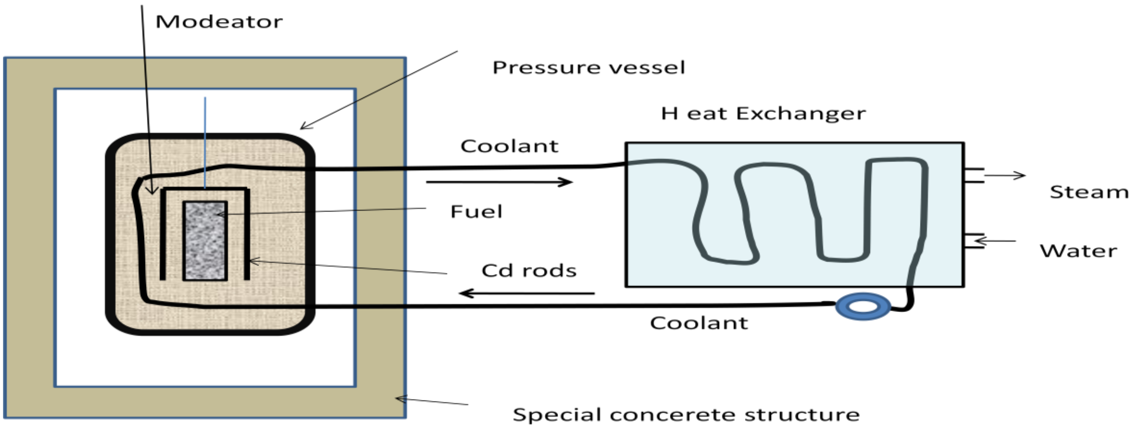


Fig. Diagrammatic sketch of a thermal nuclear reactor

2. Fast breeder reactors:

In these reactors, the moderators are not used. then on fashionable $^{238}U^{92}$ is used as a fuel. The fast neutrons produced in the fission of ^{235}U are used to convert the the non fashionable 238 U into fissionable ^{239}Pu, as shown above. The plutonium produced undergoes fission and even by slow neutrons. More plutonium is produced when is used in fission, hence the name fast breeder reactor.

The non fissionable $^{232}Th^{90}$ can also be used as a fuel. Irradiation of this fuel in fast breeder reactors with neutrons produces $^{233}U^{92}$, as shown below:

$$^{232}Th_{90} + {}^{1}n_{0} \longrightarrow {}^{233}Pa_{91} + {}^{0}_{-1}e$$

$$^{233}_{91}Pa \longrightarrow {}^{233}_{92}U + {}_{-1}e^{0}$$

$^{233}U_{92}$ produced as above can be fissioned as usual by slow neutrons. In this type of reactor, the coolant is the same as used in thermal reactors. However, a pressurized water reactor has also been designed in which water under high pressure is used as a coolant.

Disposal of radioactive waste from nuclear reactors: Radioactive waste is any waste material radioactive exceeds certain limits established by the regulations of the international Commission on radiation protection (ICRP). the intention of regulations controlling the release of radioactive waste from nuclear installations is to keep the level of radioactivity in the environment will be below the levels are recommended by the ICRP.

The radioactive wastes are classified into two types: those of low activity and those of higher activity. For low activity wastes, Shallow burial is considered adequate.in this technique, the low activity solid waste is buried into the sea beds in coastal areas. for high activity wastes, deep sea burial is essential. in this technique holes are drilled into the bottom of the deep sea which are then filled with the solid waste and sealed properly. the water covering the disposal site acts as an additional barrier between waste and human beings. Alternatively, the high activity solid waste which generally consists of waste oxides is fused with additives such as SiO_2, B_2O_3, Al_2O_3, Na_2O and CaO. on solidification, the melt forms a glass with good stability. e the glass material thus obtained is filled in a steel containers which are embedded in rocks, rock salt, granite for shale.

Liquid nuclear wastes which consist of aqueous solutions or sludges are disposed off as follows: The volume of the waste is a first reduced by evaporation, ion-exchange or flocculation. the residual material is filled in stainless steel containers which are then buried deep underground.

Some exotic alternative to get rid of radioactive waste that are occasionally mentioned are the disposal of the waste into the earth's ice caps or into outer space. It is, however, doubtful if these disposal techniques would be as safe as anticipated.

Classification of reactor:

There are three types of reactors

1. breeder reactor
2. nuclear fusion
3. Stellar energy

5.11 Nuclear Fusion

The process which involves the fusion are combination of two lighter nuclei to give a somewhat heavier and more stable nuclei with the Liberation of tremendous amount of energy is known as nuclear fusion. this is the principle of hydrogen bomb. the two light nuclei employed for the purpose are the isotopes of Hydrogen, i.e. deuterium ($_1H^2$) and tritium ($_1H^3$),

$$_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1 + \text{energy}$$

The positively charged atomic nuclei on account of the forces of repulsion do not fuse at ordinary temperatures. At very high temperature, the nuclei may have sufficient energy to overcome the forces of repulsion and thus they fuse. these reactions are, therefore, also called thermonuclear reactions. The high temperature needed is brought about by a bomb of fission type.

The energy of the sun is also due to fusion of hydrogen atoms to form a stable helium nuclei.

$$2\,{}_1H^1 \longrightarrow {}_1H^2 + {}_{+1}e^0 + \text{energy}$$

$$_1H^2 + {}_1H^1 \longrightarrow {}_2He^3 + \text{energy}$$

$$2\,{}_2He^3 \longrightarrow {}_2He^4 + 2\,{}_1H^1 + \text{energy}$$

$$4\,{}_1H^1 \longrightarrow {}_2He^4 + 2\,{}_{+1}e^0 + \text{energy}$$

in these reactions, there are also occurs a loss of mass which is responsible for the Liberation of tremendous amount of energy given by the Einstein relation, $E=mc^2$. However, the loss of mass in this case is greater than in the fission reactions.

Calculation of energy released in nuclear fusion:

Let us write the reaction involving the fusion of four hydrogen nuclei to form Helium nucleus.

$$4\,{}_1H^1 \longrightarrow {}_2He^4 + 2\,{}_{+1}e^0$$

Hydrogen Helium Positron

Mass: 4×1.00814 4.0039 $2\times 0.0005 = 0.001$

or, 4.0337amu $= 4.0049$amu

$\therefore$ Loss in mass, $\Delta m = (4.0337 - 4.0049)$ amu $= 0.028887$ amu

$\therefore$ Energy released $= 0.028887 \times 931.5$ Mev $= 26.82$Mev

$\therefore$ Energy released/g of hydrogen consumed $= \frac{26.82}{4} = 6.205$ MeV

$= 6.205 \times 2.3 \times 10^7 = 1.42 \times 10^8$ kcal.

Nuclear fusion reactions in stars:

The energy source of stars, including the sun is believed to be derived from a complex chain of nuclear reactions which on the whole represents the combination of 4 hydrogen atoms to form 1 Helium atom. this can occur as follows in two ways.

a. **Carbon cycle:**

Carbon cycle occurs in the environment of stars and ultimately to the fusion of four hydrogen nuclei to form one Helium nucleus with the production of tremendous amounts of energy. the various steps are as follows:

$${}_6C^{12} + {}_1H^1 \longrightarrow {}_6C^{13} + \gamma + Q_1$$

$${}_7N^{13} + {}_1H^1 \longrightarrow {}_6C^{13} + {}_{+1}e^0 + {}_0\vartheta^0 \text{ (neutrino)}$$

$${}_{6}C^{13} + {}_{1}H^{1} \longrightarrow {}_{7}N^{14} + \gamma + Q_{2}$$

$${}_{7}N^{14} + {}_{1}H^{1} \longrightarrow {}_{8}O^{15} + \gamma + Q_{3}$$

$${}_{8}O^{15} \longrightarrow {}_{7}N^{15} + {}_{+1}e^{0} + {}_{o}\vartheta^{0}$$

$${}_{7}N^{15} + {}_{1}H^{1} \longrightarrow {}_{6}C^{12} + {}_{2}He^{4}$$

$$4\ {}_{1}H^{1} \longrightarrow {}_{2}He^{4} + 2\ {}_{1}e^{0} + 2\ {}_{o}\vartheta^{o} + (Q_{1} + Q_{2} + Q_{3})$$

the value of (Q1+ Q2+ Q3) is nearly 24.7 MeV. the destruction of positron further gives an extra energy of 2MeV. So, a total of 26.7 MeV energy is released per carbon cycle. it has been estimated that nearly 6 million years are required for the completion of a single cycle and approximately temperature of 2 x 10 7 degree centigrade is necessary to occur.

b. Proton-Proton chain reaction:

as mentioned earlier, Proton Proton fusion lead to the formation of helium nuclei which leads to an evolution of 26.7 MeV of energy.

Controlled Nuclear Fusion:

Unlike the fission process, diffusion process could not be controlled. Since there are an estimated 10-17 pounds of deuterium $({}_{1}H^{2})$ in the water of the earth, and as each pound is equivalent in energy to 2.00 tons of coal, controlled fusion reactor would provide a Virtually inexhaustible supply of energy. Thus, tremendous efforts have been made to construct such a reactor, and it is hoped that success is not too far in the future.

The following four main things are to be solved in obtaining useful energy from fusion process:

1. A suitable fuel must be available. This involves the separation of deuterium from ordinary water or the production of tritium in a nuclear reactor.
2. The particles must be heated to temperatures ranging from 50 to 100 million degrees depending upon the particular reaction.
3. The state of Plasma* must be present for a long period of time. This is done to allow a substantial portion of the nuclei present in it to undergo fusion.
4. Now the problem is how to harness the released energy in order to generate useful power.

*Materials at high temperatures required in the fusion process have no longer electrons at their atoms and thus the high temperature system is referred to as plasma.

Radiation chemistry

5.12 Elementary idea about radiation chemistry

In recent years another branch of chemistry, known as radiation chemistry, has also been developed. it deals with the reactions which take place whenever a substance is exposed to very high energy radiations such as grammar is. this process is also known as radiolysis.

Radiolysis involves the following two stages :

Primary stage: in the primary stage, the exposure of the substance to high energy radiations results in the ionization of the substance to form ions and electrons. Thus,

$$\text{□} \xrightarrow[\text{□□□□□□□□□□}]{\text{□□□□ □□□□□□□}} A^+ + e^-$$

Secondary stage:

in the secondary stage, the ions and the electrons give rise to a variety of reactions sum of which are summed up below:

a. Formation of excited molecule:

$$\underset{}{A^+ + e^-} \longrightarrow \underset{\text{[excited molecule]}}{A^*}$$

b. Capture of the released electron by a molecule M to form M- ion:

$$M + e^- \longrightarrow M$$

c. Interaction of Ions A+ and M- to give excited molecule :

$$A^+ + M^- \qquad A^* \quad + \quad M$$

[excited molecule]

d. decomposition of the excited molecule A* into free radicals X and Y or to give stable molecules B and C.

$$A^* \begin{cases} X. + Y. \ \text{(Free radicals)} \\ B + C \ \text{(Stable molecule)} \end{cases}$$

e. Decomposition of ion A+ into another ion R+ and free radical X or an ion B+ and a stable molecule C.

$$A^* \begin{cases} R^+ + X. \ \text{(Free radicals)} \\ B^+ + C \ \text{(Stable molecule)} \end{cases}$$

The free radicals produced as above may initiate other chain reactions .

5.13 **Radiolysis of Water and Aqueous Solutions**

Radiolysis of water vapour by Gamma radiations afford one of the best examples for studying the subject of radiation chemistry. the major products of radiolysis of water vapour are free radicals, .H, OH, HO_2 ; to positive ions H_2O^+, H_3O^+, H^+, OH^+ ; hydrated electron e-(aq) and Molecular species H_2 and H_2O_2. the species formed initially by radiation give rise to another product by secondary reactions. The variety of products formed by radiolysis of water are described below in some detail.

Formation of ionic products:

Some of the ionic products produced during radiolysis of water are as follows:

$$\gamma + H_2O \longrightarrow H_2O^* \longrightarrow H_2O^+ + e^- \text{ (excited species)}$$

$$e^- + H_2O \longrightarrow H^+ + .OH + 2e^- \longrightarrow H_2O^+ + 2e^-$$

$$e^- + H_2O \longrightarrow OH^{\cdot} + .H + 2e^- \longrightarrow H_2O^+ + 2e^-$$

$e^- + H_2O \longrightarrow O^+ + H_2 + 2e^-$

$H_2O^+ + H_2O \longrightarrow H_3O^+ + .OH$

The electrons formed either recombine with positive ions as well as straight above or get solvated as shown below:

$e^- + H_2O \longrightarrow e^- (aq).$

The various ionic products formed can be detected in a mass spectrometer. The relative abundance of the ionic products is: (fig) . Thus,H_2O^+ is the main ionic product of radiolysis of water vapour.

Formation of free radicals:

The ionic products obtained as above are very reactive. They combined to yield free radicals.

$H_2O + e^- \longrightarrow .OH + .H$

$H^+ + H_2O + e^- \longrightarrow H_3O^+ + e^- \longrightarrow 2H. + .OH$

$OH^+ + H_2O + e^- \longrightarrow .H + 2.OH$

The per hydroxyl radical OH_3 is also formed in the presence of dissolved air or oxygen.

$.H + O_2 \longrightarrow .HO_2$

Formation of molecular products:

The free radicals produced above are highly reactive. they recombine among themselves to stable molecular products:

$.H + .OH \longrightarrow H_2O$

$.H + .H \longrightarrow H_2$

$.OH + .OH \longrightarrow H_2O_2$

$.OH + .HO_2 \longrightarrow H_2O + O_2$

$$.O_2H + .HO_2 \longrightarrow H_2O_2 + O_2$$

Reaction between molecules and free radicals:

Experimental conditions are favourable reactions between molecules and free radicals take place leading to chain reactions.

$$.H + H_2O_2 \longrightarrow .OH + H_2O$$

$$.OH + H_2 \longrightarrow .H + H_2O$$

(regenerated)

It may be mentioned that all secondary reactions and water radiolysis are due to the free radical since the ionic products are short lived and the molecular products are inert. Therefore, the secondary reactions can be eliminated by eliminating, i.e, by scavenging the free radicals by the addition of suitable substances known as scavengers. These substances, which are added only in trace amounts, interact and destroy specific free radicals. For instance, deuterium scavengers quantitatively both H and OH radicals, as follows:

$$.H + D_2 \longrightarrow .D + HD$$

$$.OH + D_2 \longrightarrow .D + HOD$$

$$.D + .D \longrightarrow D_2 \text{ (at the walls of the container)}$$

Hydrated electron:

Irradiation of water by X-rays or Gamma Rays results in production of electron of high energy they lose a part of their energy in collisions and are letter to become thermalized. The thermalized electrons get hydrated yielding intensely coloured hydrated electrons e- (aq), exhibiting a broad absorption spectrum with maximum at about 7200 angstrom.

The hydrated electron is highly reactive. It readily reacts with water as well as with H^+ ions.

$$e^-(aq) + H_2O \longrightarrow H + OH^-$$

$$e^-(aq) + H^+ \longrightarrow H$$

It acts as a reducing agent and gives the same products as given by H atoms in many cases. For example,

$$Cu^{2+} + e^{-}(aq) \longrightarrow Cu^{+}$$

$$[Cu^{2+} + H \longrightarrow Cu^{+} + H^{+}]$$

5.14 Radiolysis of some aqueous solutions

Radiolysis of several Aqua solutions of acid, basis, Salts and redox system have been studied and probable mechanism for the radiolytic process have been proposed. A few cases have been discussed below:

1. Radiolysis of Fricke dosimeter solution:

   The Fricke dosimeter solution consisting of 0.01M $FeSO_4$ in 0.4M H_2SO_4 in the presence of dissolved air has been extensively studied for its radiolysis. The following mechanism has been proposed for the oxidation of Fe^{2+} to Fe^{3+} ion in the Frieck dosimeter described on the next page.

$$Fe^{2+} + .OH \longrightarrow Fe^{3+} + OH^{-}$$

$$Fe^{2+} + .HO_2 \longrightarrow Fe^{3+} + .OH^{-}{}_{2}$$

$$.OH_2^{-} + H^{+} \longrightarrow H_2O_2$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + .OH + OH^{-}$$

The free radicals and OH and HO_2 required above are produced as shown earlier.

2. Radiolysis of redox systems using energy transfer from irradiated alkali halides: Sometime, instead of directly exposing the substances to Gamma radiation, the energy transfer from irradiated alkali halides is used to bring about radio listeners. for example, when the Gamma irradiated sodium chloride is added to a solution of a Redox system, the radiolytic reaction is found to occur at room temperature. Thus, the Redox reaction between BrO3- and I- ions takes place in the presence of irradiated NaCl.

$$\underset{}{BrO_3^-} + \underset{(1M)}{3I^-} \xrightarrow{NaCl^*} \underset{(1mm)}{Br^-} + \underset{(17\%)}{I_2} + \underset{(10\%)}{IO_3^-}$$

When the irradiated NaCl is dissolved in water, the following species are produced:

$e^-(aq)$, .H and .Cl. They react with I^- and BrO_3^- ions as follows:

$$.Cl + I^- \longrightarrow Cl^- + ½ I_2$$

$$e\text{-}(aq) + BrO_3^- \longrightarrow BrO_3^{2-}$$

$$.H + BrO_3^- \longrightarrow BrO_3^{2-} + H^+$$

Some of the free iodine liberated above is oxidised by BrO3 ^2- ions produced in third and fourth step to give IO_3^- and Br- ions:

$$BrO_3^- + I_2 \longrightarrow IO_3^- + Br^-$$

Other examples of reactions using energy transfer:

(a) Fe^{2+} (Fricke solution) $\xrightarrow{NaCl.}$ Fe^{3+}

(b) $BrO_3^- + 3NO_2^- \xrightarrow{NaCl.} Br^- + 3NO_3^-$

(c) Rhodamine - B solution $\xrightarrow{NaCl.}$ Reduced species of the dye.

(d) Xyenol orange $\xrightarrow{NaCl.}$ Reduced species.

5.15 Radiation Dosimetry (Fricke's Dosimeter)

In order to fully understand a reaction induced by radiation, it is important to know the amount of energy used and the yield of the products. These data help in the formulation of the mechanism involved in the reaction. We can use any change, physical or chemical, induced by radiation in a substance as a measure of the energy transformed to the substance provided the magnitude of the change is directly proportional to the dose and is independent of the dose rate and the nature of the radiation. the physical method employed for dosimetry involve measurement of ionization produced in a gas or photographic blackening or direct colorimeter. this is called physical dosimeter. in chemical dosimetry, with which we are concerned here, we investigate the year is obtained in chemical reactions and used by radiations. two chemical dosimeters which are in common use are described below:

1. The Fricke dosimeter:

   This dosimeter is based on the study of oxidation of Fe^{2+} to Fe^{3+} ions. The Fricke solution is obtained by dissolving 0.4 G of Mohr salt ((fig)),0.06gof NaCl and 22 ml of concentrated H_2SO_4 in distilled water (dissolved air being present) and making the volume to 1 litre (NaCl* stands for Gamma irradiated NaCl). a portion of the solution is taken in a thick container and exposed to Gamma radiation for a certain period of time. Fe^{2+} is oxidised to Fe^{3+}* ions (as per mechanism given earlier). The presence of NaCl only facilitates the Oxidation reaction. The the concentration of Fe3+ of Ions produced is determined spectrophotometrically at a wavelength of 3040 angstrom, i.e., 340 NM. The concentration of Fe^{3+} ions can also be determined by plotting optical density versus concentration of Fe^{3+} ions. knowing that the standard yield of Fe^{3+} ions is 15.5 ions per 100 MeV in energy absorbed, the unknown dose can be estimated from the measured concentration of Fe^{3+} ions.

2. The ceric sulphate dosimeter: in the decimeter, a 1-10mM solution of acidified ferrous sulphate is exposed to Gamma radiation for a given period of time. the Ce^{4+} is reduced to Ce^{3+}. The fall in concentration of Ce^{4+} Ions is determined spectrophotometrically at 320 nm. This decimeter is particularly useful for measuring high doses. However, it is very sensitive to the presence of organic impurities. This dosimeter is generally calibrated against the Fricke dosimeter.

5.16 Units of Radiation Energy

Several units have been proposed for expressing the dose or the amount of energy absorbed by the irradiated substance. the different dose units with their conversion equivalents are given below:

The Rad:

Is the most common unit of dose absorbed. It is defined as 1 rad (r) equals absorption of 100 erg of energy per gram of the substance = 10 - 5 J/g.

$$= 6.24\times 10^{13} eV/g \ (leV= 1.602 \times 10^{19} j)$$

If the largest substance is a liquid of density ρ:

$$1\text{r} = 6.24\times10^{13}\rho\ \text{eV/cm}^3.$$

The Gray:

the grey is the SI unit of those defined as 1 Gray (GY)= 1J kg-1= 100 rads.

The Rontgen:

The Rontgen (R) is the physicist unit of exposure, dose, and this is based on the ability of the radiation to ionize air. The Rontgen is defined as exposure to such a dose that would produce in 1cm3 of dry air STP (= 0.01 293g) ions carrying 1 esu of electricity of either sign (not both) generally

$$1\text{R(air)} = 0.87\text{rad} = 8.7\text{mGy}.$$

The RBE:

RB stands for relative biological effectiveness of a given type of radiation. The biologists recognise the differences in effectiveness of different types of radiation in their action on live tissues and they have graded them as-

$$\text{RBE} = 1 \text{ for X- rays, } \beta \text{ -rays and } \beta\text{– particles}$$

$$= 2.5 \text{ for thermal neutrons,}$$

$$= 10 \text{ for } \alpha\text{– particles, fast neutrons and protons.}$$

The REM:

REM stands for rontgen equivalent mammal.

This is given by product of RBE X Rad.

The Sievert:

It is the SI unit of rem:

$$1 \text{ Sievert (SV)} = \text{RBE} \times \text{ grays}$$

$$= 100 \text{ rem.}$$

5.17 Summary

Nuclear Chemistry: it is that branch of chemistry which deals with the phenomena involving the nuclei of atoms.

Radioactivity: it is the phenomena spontaneous emission of certain kinds of radiation by some elements the elements emitting such radiation are called radioactive elements.

Representation of Nuclear Reactions:

reactant nucleus (bombarding particle, particle emitted) product nucleus this is known as Bethe notation some examples are given below :

(fig)

nuclear fission: it is the splitting of a heavy atom like that of Uranium 235 into a number of fragments of much smaller mass buy bombardments with subatomic particles with Liberation of fusion energy.

(fig)

nuclear reactor: it is an arrangement in which the energy produced in the form of heat in a nuclear fission, can be used in a controlled manner steam which can run the turbine and produce electricity.

control rods:

in the reactor core, the fuel rods are of U-235, control rods are of Cd or B.

Moderator: it is used to slow down the speed of neutrons. These are heavy water or graphites.

Coolants: they are used to carry away the heat. These are heavy water or molten sodium or alloy of Sodium and potassium.

breeder reactors: these are the reactors in which the neutrons produced from the fission of U-235 are partly used to carry on the fission of U-255 and partly used to produce some other fissionable material e.g Pu- 235 from U- 235.

nuclear fusion: it is the process in which lighter nuclei there fuse together to form heavier nucleus. Thus take place at extremely high temperatures (~_ 10 6 K) i.e. in the sun.

5.18 Terminal Questions

Q. Radio listeners of water yields hydrogen according to the reactions

$$2\ H_2O \rightarrow H_2 + H_2O_2$$

Calculate the volume of hydrogen produced per hour in 2000 kn reactor. the yield of hydrogen is 1.7 molecule per 100 eV of energy absorbed.

UNIT 6: BIOENERGETICS

6.1. Introduction

The life of plants and animals is maintained by various types of biological reactions taking place in their cells. Although, these biological reactions are complex organic reactions catalyzed by various types of enzymes. But their physical aspects cannot be ignored. The plants and animals take food. These digested and generate energy in the form of ATP. Thermodynamics involved in the respiration can be explained on the basis of Gibbs free energy. The biological energy is in the form of ATP. The most important step of respiration is glycolysis. The glycolysis produces 36 ATP

Objectives:

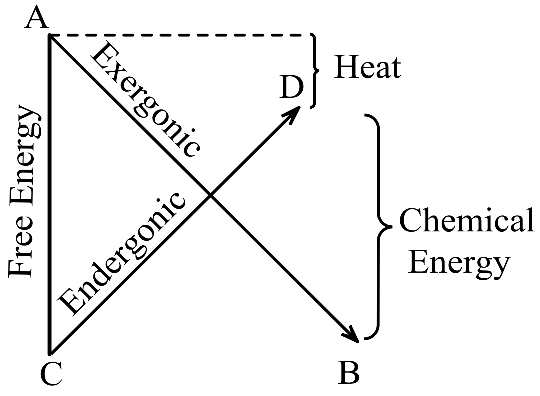
After studying this unit, you should be able to:

- Explain the biological application of thermodynamics.
- Explain the biological application of high energy compounds.
- Explain how biological energy is generated.
- Explain why ATP is regarded as currency of force energy.
- Explain various steps involved in glycolysis.
- How a single molecule of glucose generates lots of energy in the cell.
- How the thermodynamics is related to biology

6.2. Brief idea about bioenergetics

Thermodynamics is the branch of physical chemistry that deals with energy changes. And biochemical thermodynamics (or biochemical energetics or bioenergetics, as it is also called) is the field of biochemistry concerned with the transformation and use of energy by living cells. The chemical reactions occurring in living beings (or biochemical reactions) are associated with the liberation of energy as the reacting system moves from higher to lower energy level. Most often, the energy is liberated in the form of heat. In non biologic systems, heat energy may be transformed into mechanical or electrical energy. Since the biologic systems are isothermic, the heat energy cannot be used to drive the vital process (such as synthesis, active transport, nerve conduction, muscular contraction etc.) obtain energy by chemical linkage (or coupling) Fig.1 coupling of an exergonic oxidation reactions. The simplest loan endergonic type of coupling (Fig.1) may be represented reaction by the equation.

$$A + C \longrightarrow B + D + Heat$$



$$A + C \longrightarrow B + D + Heat$$

(Fig.1)

The conversion of metabolite A to metabolite B occurs with the release of energy. It is coupled to another reaction, where energy is convert metabolite C to metabolite D.

Biological applications:

a. The Biomass, consisting of all the living matter of the universe, constitutes and open non-equilibrium system which derive the matter and energy from its surrounding for use in life processes and also eliminates them to the surroundings. Each individual organism in the Biomass constitutes and open, steady-state, non-equilibrium system which maintains its steady-state by exchanging matter and energy with its surrounding so as to balance its gain and losses from and to the latter. Photosynthetic plants, for example, gather light photons, water and CO2 from their surroundings, use them and synthesizing bio-molecules and simultaneously eliminate O_2 to the surroundings; animals collect nutrients as bio-molecules basically synthesized by plants using matter and energy from their surroundings. All living organisms subsequently catabolize some of their bio-molecules using O_2 from the surroundings, eliminate water, CO_2, other catabolite and also some heat to the surroundings, and utilize the rest of the generated energy and bio-molecules to delay their own decay to the ultimate thermodynamics equilibrium at death. Life is thus maintained as a steady state of non equilibrium by the influx of energy packets into the system other as light photons or as nutrients synthesized with their help, by their use in forming bio molecular bond energies, and by the ultimate outflow of both energy and matter to the surroundings.

b. A spaceship with its astronauts behaves practically as an isolated system, well insulated against matter and energy exchanges with the surrounding space. But the astronaut inside the spaceship constitutes an open system exchanges matter and energy freely with surrounding spaceship space to maintain non-equilibrium steady state tells the exhaustion of nutrients and other Irreversible changes.

6.3. Gibbs free energy

Gibbs free energy (G) is that fraction of the total energy of a system, which can perform work or change into an equivalent amount of another form of usable energy (not heat) in a system driving towards thermodynamics equilibrium at constant temperature, volume and pressure. It amounts the difference between Enthalpy (H) and the product of Entropy (S) and Absolute Temperature (T).

$$G = H - TS$$

Under isothermal conditions, the change in free energy (ΔG) of a system is less than the enthalpy changes (ΔH) because a part of the letter is unavailable for work due to entropy.

$$\Delta G = \Delta H - T\Delta S \quad \text{Or, } \Delta H = \Delta G + T\Delta S$$

A negative ΔG means a fall in the free energy during a process or chemical reaction and involves an increase in entropy. Such a process or a reaction, called exergonic, can take place spontaneously, though often very slowly, and has high equilibrium constant. A negative ΔG of high magnitude indicates an irreversible reaction.

A positive ΔG means a rise in the free energy and a fall in entropy during a process or reaction so that the latter has to occur in a direction lowering entropy and cannot take place spontaneously. Such chemical reaction or process is called endergonic, possess low equilibrium constants, and can occur only if coupled with exergonic reaction having a larger negative ΔG. As a chemical reaction (or a process of transport) with negative ΔG proceeds spontaneously towards equilibrium, the magnitude of ΔG falls progressively because it varies at a logarithmic rate with the ratio of concentration of products and reactants. Finally, ΔG reaches 0 when the system attains equilibrium and can neither perform work not change spontaneously any further. Supply of some free energy to the system can still make the reaction proceed further and away from the state of equilibrium.

Standard free energy change (ΔG^o) of a chemical reaction is the change in free energy during the change of 1 mole of each reactant to 1 mole of the respective product under specified and constant standard condition, viz, 298 K (25^oC), 760mm Hg pressure and 1.0 M concentration of each reactant or product in an aqueous solution. It is a constant for a specific chemical reaction under standard conditions and is given by the sum of ΔG^o values for formation of the products from their elements, less the sum of ΔG^o values for such formation of the reactants.

$$\Delta G^o = \Sigma\Delta G^o \text{ product} - \Sigma\Delta G^o \text{ reactants}$$

ΔG^o is an exponential function of the equilibrium constant K_{eq} of a chemical reaction. Where R is the molar gas constant, T is the absolute temperature, [C] and [D] are the molar concentration of products, and [A] and [B] the molar concentration of reactants,

$$\begin{aligned} \Delta G &= \Delta G^o + RT\log_e K_{eq} \\ &= \Delta G^o + 2.303RT\log_{10}K_{eq} \\ \therefore \Delta G^o &= \Delta G - 2.303RT\log_{10}K_{eq} \end{aligned}$$

As ΔG falls to 0 at the thermodynamics equilibrium, ΔG^o becomes independent of ΔG in that state and amounts to:

$$\begin{aligned} \Delta G^o &= -2.303RT\log_{10}K_{eq} \\ &= 2.303RT\log_{10}\frac{[C] \text{ x } [D]}{[A] \text{ x } [B]} \end{aligned}$$

Thus, if $K_{eq} > 1$, ΔG^o is negative, is $K_{eq} < 1$, ΔG^o is positive. ΔG is higher or lower than ΔG^o according to the relative concentrations of the product and reactants.

$\Delta G^{o'}$ represents the standard free energy change at pH 7, all the standard conditions of temperature, concentration and pressure being identical with those specified for ΔG^o. When a series of chemical reactions occur in an ordered sequence with the products of each reaction serving as the reactants of the next, $\Delta G^{o'}$ of the entire series is the algebraic sum of the individual $\pm \Delta G^{o'}$ values ($\pm \Delta G_i^{o'}$) of all the reactants of the series.

$$\Delta G^{o'} = \Sigma\Delta G_i^{o'}$$

An endergonic reaction with the positive ΔG^o can take place only if it is coupled with an exergonic reaction with a larger negative ΔG^o, because the sum of the free energy changes of the two coupled reactions gives a negative overall ΔG^o for driving the endergonic reaction, and is largely captured as the bond energy of its products.

During the transmembrane flow of an ion from a solution of concentration C_1 to a solution of concentration C_2, the work done equals the free energy change during the process.

$$\Delta G^o = -RT\log_e \frac{C_1}{C_2} = +2.303RT\log_{10} \frac{C_2}{C_1}$$

When an ion is transported down its concentration gradient (i.e $C_1 > C_2$), $\log[C_1/C_2]$ is negative and so is the ΔG^o also. The negative ΔG^o indicates that such a transport can take place spontaneously - by diffusion - without any energy expenditure.

But where the ion is transported against its concentration gradient (C_2/C_1), $\log[C_2/C_1]$ and hence ΔG^o are positive, the positive ΔG^o indicates that the ion cannot be transported across the membrane by diffusion, and requires coupling with a suitable exergonic process for the supply of additional energy for its transport.

ΔG, ΔG^o and $\Delta G^{o'}$ are all expressed in J, cal or Kcal mol^{-1}.

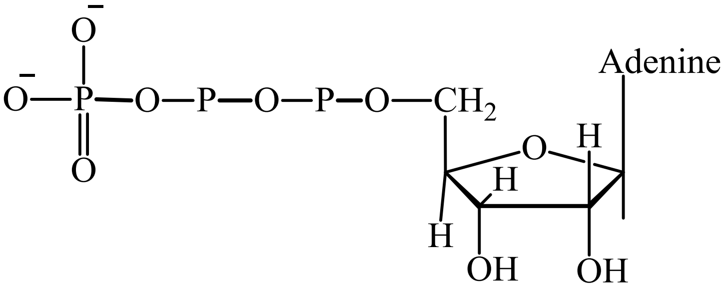
6.4 Study of energy transformation in living system (bio-energetics) high-energy compounds

Such compounds are called high energy compounds as possess one or more covalent bonds with negative $\Delta G^{o'}$ of hydrolysis amounting to -7 KCal/mol or still higher in magnitude; such bonds are known as high energy bonds in contrast to other bond having negative $\Delta G^{o'}$ of lesser magnitudes. For example, while innermost α-phosphate bond of ATP, a puring nucleoside tri-phosphate, is a “low energy” bond ($\Delta G^{o'}$ = -3.4KCal), its terminal γ and the next inner β-phosphate bonds are high energy bonds.

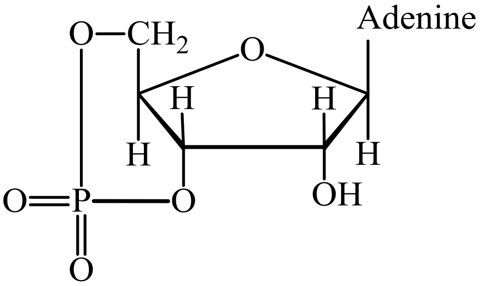
High energy bonds occur in several classes of compounds such as phosphoric anhydrides like higher purine/ pyramid nucleotides (e.g, ATP, ADP, GTP, GDB, CTP, UTP and CDP), enol phosphates like phosphoenolpyruvate, acyl phosphates like 1, 3 bi-phosphoglycerate, phosphoguanidines like creatine phosphate, thiol esters like succinyl-CoA, sulfonium compounds like S- adenosylmethionine, cyclized nucleotides like cyclic AMP, and sulphuric phosphoric anhydrides like adinosine 3’- phosphate 5’-phosphosulphate (Fig.1). The high negative $\Delta G^{o'}$ values of these compounds result largely from:

a. Their thermodynamics liability owing to (i) high electrostatic repulsion between the anionic groups on two sides of high energy bond, and (ii) high completing resonances because of attractions between central group and the groups on two sides of that bond.

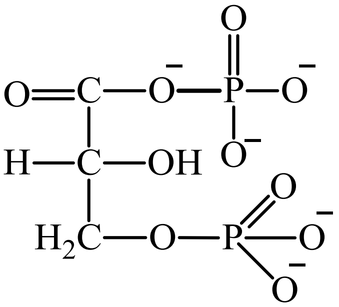
b. Their kinetic stability due to structural features respecting their exceptionally high resonances.



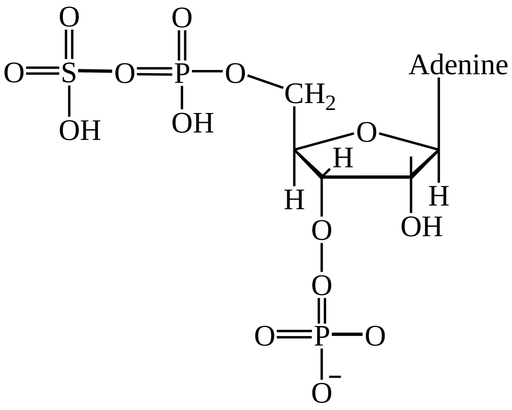
Adenosine triphosphate



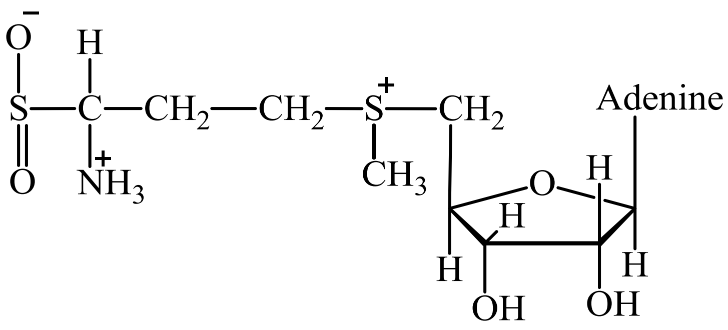
Cyclic AMP



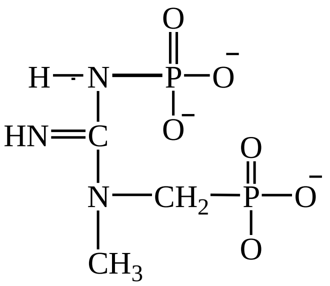
1,3 - Biphosphoglycerate



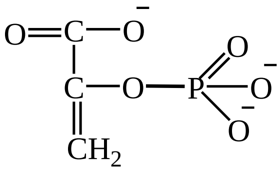
Adenosine 3'-phosphate
5'-phosphosulfate



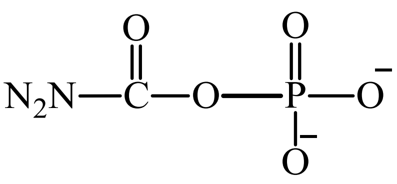
s-Adenosylmethionine



Creatinephosphate

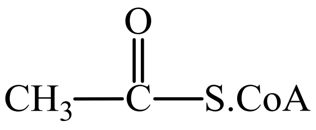


Phosphoenolpyruvate



$$N_2N-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P}}-O^-$$

Carbamoyl Phosphate



$$CH_3-\overset{\overset{O}{\|}}{C}-S.CoA$$

Acetyl-CoA

Fig.1. Some high energy compounds.

Some high energy nucleotides such as ATP and GTP lie midway in the sequence of bio-molecules in order of their $\Delta G^{o'}$ values and consequently play significant roles in energy transductions.

Some high-energy cyclic nucleotides such as a cyclic AMP and cyclic GMP participate in transduction of signals brought by specific hormones like adrenaline to the target cells.

Biological applications

a. Exergonic reactions can take place spontaneously, but many of them at too slow rates at the body temperature to be perceptible. Such exergonic reactions need to be catalyzed in vivo by enzymes which increase their velocities but do not alter their $\Delta G^{o'}$ or K_{eq}. But endergonic reactions require not only enzymes but also a coupling with appropriate exergonic reactions for the supply of additional amount of free energy.

b. The $\Delta G^{o'}$ of hydrolysis of ATP to ADP and Pi amounts to more than -7 Kcal mo^{-1}. In the living body, this exergonic reaction is a frequently coupled with the different endergonic reactions having positive $\Delta G^{o'}$ of lower magnitudes, such as phosphorylation of choline, glucose and glycerol, anti gradient transmembrane transports like that of Na^+, synthesis of many substances like nucleic acid and proteins, nerve conductions and muscle contractions. The hydrolysis of ATP serves as a source of a free energy for driving such endergonic reactions against entropy.

c. The synthesis of ATP from ADP and Pi is also an endergonic reaction, driven by being coupled with some exergonic metabolic reactions having a much larger negative $\Delta G^{o'}$. Such exergonic reactions include the conversion of phosphoenolpyruvate to enolpyruvate, and the exergonic flow of electrons from NADH molecular O_2 with the help of mitochondrial electron transport chain. A major part of the free energy from these exergonic reactions remains stored as the phosphate bond energy of the ATP produced, to be used subsequently in driving other endergonic reactions as cited above. ATP, GTP, UTP and CTP may thus function as energy transducers or intermediate carriers of energy from exergonic reactions to endergonic ones.

d. Endergonic processes with positive $\Delta G^{o'}$ include active transmembrane transport against concentration gradients; e.g., active pumping out of Na^+ across the basal and lateral plasma membranes of intestinal and renal tubules respectively, and the active Na^+ efflux across nerve and muscle membranes to maintain their polarized states. Each such endergonic transport is driven by coupling it with an exergonic reaction having a high negative $\Delta G^{o'}$ like the hydrolysis of ATP. The osmotic work done in such anti-gradient transport of each mole of Na^+ is given by:

$$\Delta G^{o'} = 2.303 RT \log \frac{[Na^+]\ \text{outside}}{[Na^+]\ \text{inside}}$$

6.5. ATP as universal currency of free energy in biological systems

The living objects require a continuous supply of free energy mainly for the following for purposes:

a. To synthesize macromolecules from simpler and smaller precursors,

b. To transport molecules and ions across membranes against gradients,

c. To perform mechanical work, as in the muscle contraction, and

d. To ensure fidelity of information transfer.

The free energy in these processes is derived from environment. The phototrophs obtain this energy by trapping light energy from the sun. On the other hand, the chemotrophs obtain it by the oxidation of foodstuffs. This free energy (derived from light or from oxidation of foodstuffs) is partly transformed into a special form before it is used for biosynthesis, transport, motion and fidelity. This special carrier of free energy is adenosine triphosphate (ATP). ATP plays a central role in transference of free energy the exergonic (= energy-yielding) to the endergonic (= energy- requiring) processes in the cells. During breakdown of energy rich food stuffs or fuel molecules, some of the free energy is harnessed to make ATP from adenosine diphosphate (ADP) and inorganic phosphate (Pi), a process that requiring processes (biosynthesis, transport etc.) by undergoing a breakdown to ADP to Pi (Fig.1)

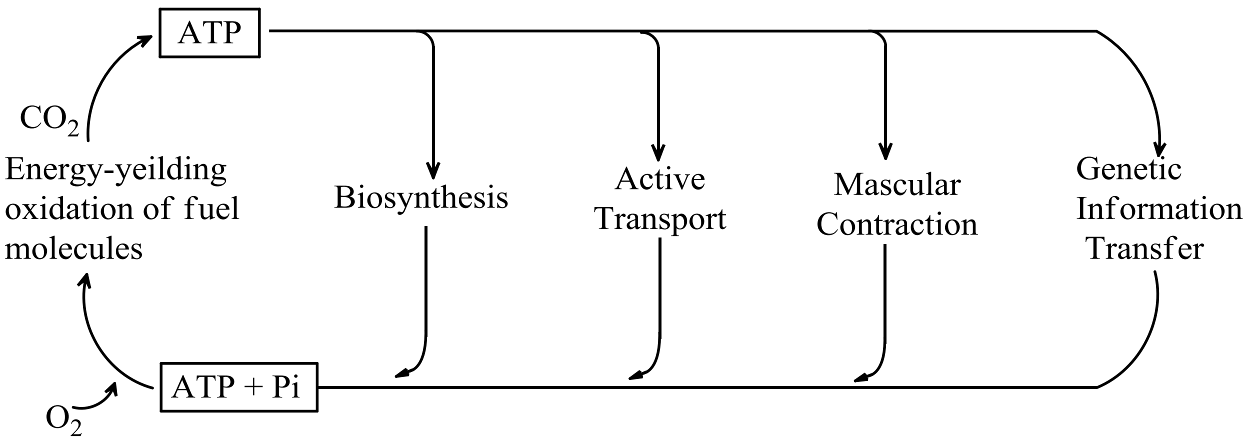


Fig.1- The ATP Cycle in Cells

Adenosine triphosphate (ATP) was discovered in extracts of skeletal muscles of Karl Lohman in Germanyand by Cyrus Fiske and Yellapragada Subbarao in the United States,

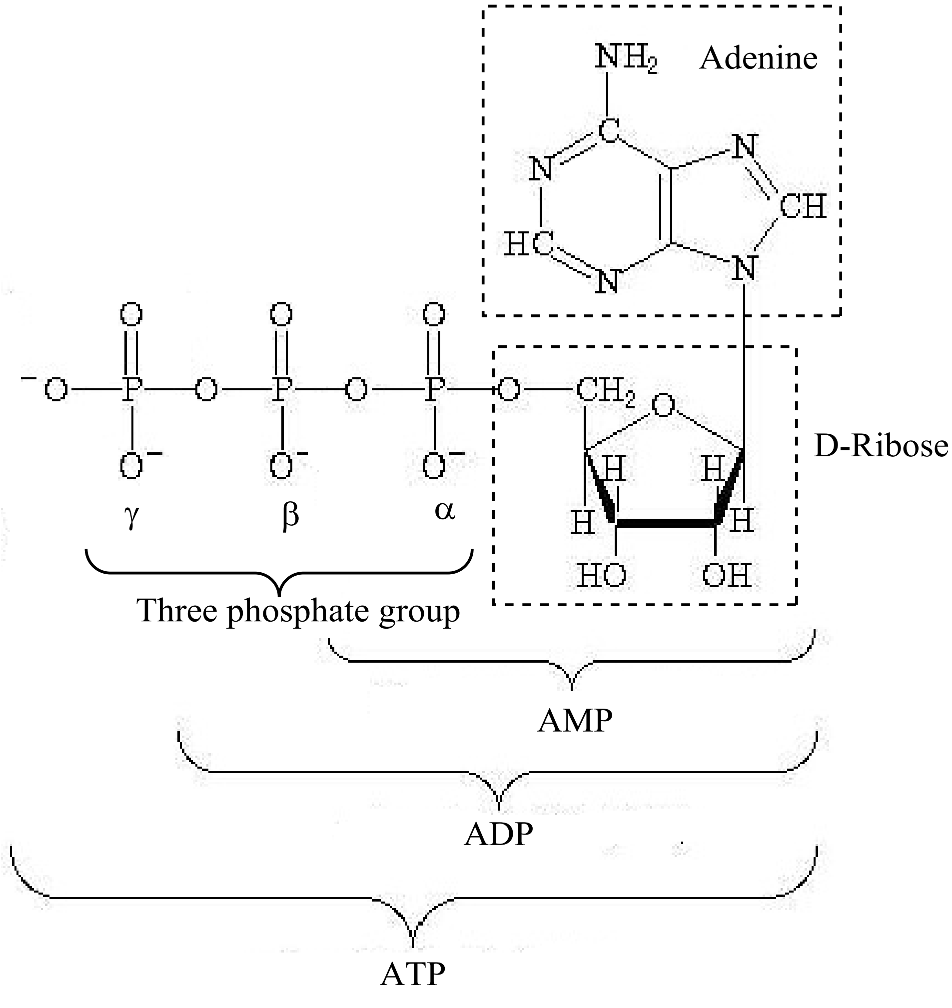
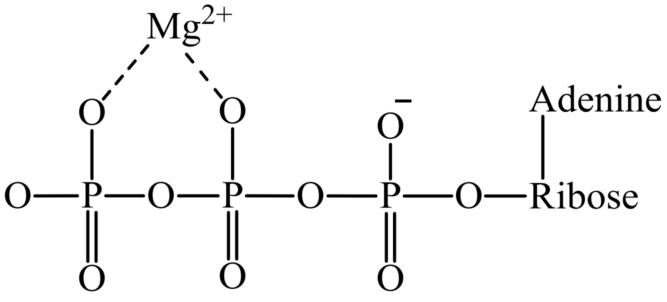


Fig.2 The structure of ATP, ADP and AMP

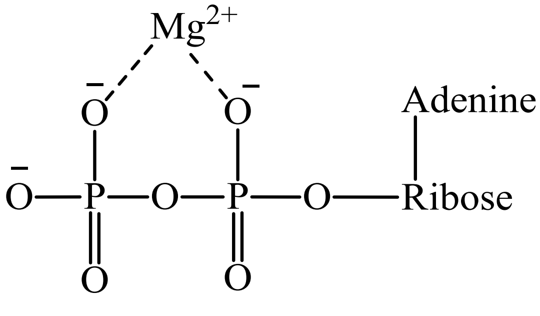
The phosphate groups of ATP are designated as α, β and γ. At pH 7.0, the phosphate groups are almost completely ionized, hence so shown here. The terminal phosphate group (i.e., y) can be enzymatically transferred to various phosphate acceptors simultaneously in 1929. Later, it was found to be present in all types of cell animal, plant and microbial. Although first thought to be concerned with muscular contraction, ATP has now been assigned many cell activities. In 1941, Fritz A. Lipmann postulated that ATP is the primary and universal carrier of chemical energy in cells. He adequately stated that the small chemical units from which the material of organisms is built “are glued together by an enormously versatile condensing reagent, ATP". He also first proposed the ATP cycle, shown in present day form in Fig.1,

Adenosine triphosphate (ATP) and its successive hydrolysis products, adenosine diphosphate (ADP) and adenosine monophosphate (AMP) are nucleotides, consisting of an adenine, a ribose and a 3, 2 or 1 phosphate group(s) respectively. ATP, ADP and AMP occur not only in cell cytosal but also in mitochondria and the nucleus. In normal respiring cells, ATP makes about 75% or more of the sum of all three adenine ribonucleotides.

At pH 7.0, the phosphate groups of ATP, ADP and AMP are almost fully ionized, so that they occur as multiple charged anions ATP^{4-}, ADP^{3-} and AMP^{2-}. But as the cell fluid contains high concentrations of MG^{2+}, The ATP and ADP both exist largely as ATP^{2-} and Mg. ADP^{-} complexes Fig.3. In fact in phosphate transfer reactions, ATP participates as its complex form. However, ATP can also form complex with Mn^{2+}.



$Mg.ATP^{-2}$



$Mg.ATP^{-}$

Fig.3 Magnesium Ion complexes of ATP and ADP

ATP serves as the principal immediate donor of a free energy in biological systems rather than as a storage form of energy. In a typical cell, and ATP molecule is consumed within a minute of its formation. The turnover of ATP is very high. For instance, a resting human consumes about 40kg ATP in a day. During strenuous labour, the ATP is consumed at rate of even 0.5 kg per minute. The endergonic processes such as biosynthesis, active transport etc., can occur only if ATP is continuously regenerated from ADP. Phototrophs harvest the free energy in light to regenerate ATP whereas chemotrophs form ATP by the oxidation of foodstuffs.

Free energy of hydrolysis of ATP and other Organophosphates:

When ATP is hydrolyzed, it loses its terminal γ-phosphate group to form ADP and organophosphate or inorganic phosphate (Pi).

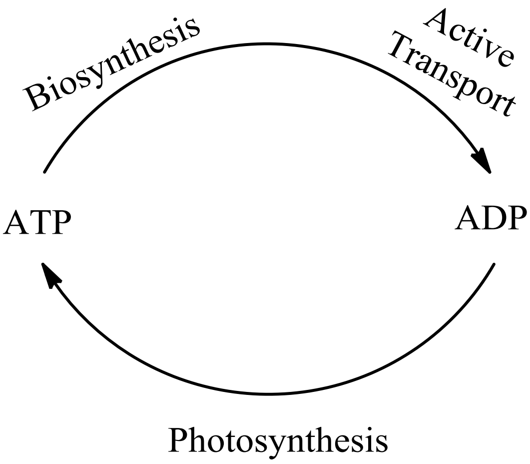


Fig.4-The ATP- ADP cycle.

Fig.4 The cycle is the fundamental mode of energy exchange in biological systems.

Standard free energy change, $\Delta G^{o'}$, energy changes have also been determined from hydrolysis of other phosphorylated compounds or organophosphates (Table 5). Some phosphates yield more and some yield less free energy than ATP upon hydrolysis, under standard conditions. This intermediate position enables ATP to function efficiently as a carrier of phosphoryl groups. Thus, with respect to the $\Delta G^{o'}$ value of hydrolysis of ATP, two classes of organophosphates are recognised: high energy phosphates exemplified by enol phosphates (e.g., Phosphoenolpyruvate), phosphoguanidines (e.g., creating phosphate and arginine phosphate) etc., which have $\Delta G^{o'}$ values larger than that of ATP and low energy phosphates, exemplified by Ester phosphates found in the intermediates of glycolysis, which have $\Delta G^{o'}$ values smaller than that of ATP. However, the designations 'high' and 'low' do not clearly indicate that there are three classes of phosphates. Such phosphates as phosphoenolpyruvate, creatine phosphate etc., whose $\Delta G^{o'}$ values are higher than that of ATP, should better be designated as 'super' high energy phosphates, the ATP then be designated as 'high' energy phosphate and the ester phosphates as 'low' energy phosphates.

Table.1 Standard free energy of hydrolysis of some phosphorylated compounds-

Compound	**$\Delta G^{o'}$ (KCal/mol)**
Phosphoenolpyruvate	-14.8
Cabamoyl phosphate	-12.3
3-Phosphoglyeroyl Phosphate or 1,3-di-phosphoglycerate (→ 3-phosphoglycerate + Pi)	-11.8
Creatine Phosphate or phosphocreatine	-10.3
Acetyl phosphate	-10.1
Arginine phosphate	-8.0
ATP (→AMP + Pi)	-7.7
ATP (→ADP + Pi)	-7.3
ADP (→AMP + Pi)	-7.3
Pyrophosphate (→2Pi)	-6.9
Glucose 1-phosphate	-5.0
Fructose 6-phosphate	-3.8
AMP (→Adenosine + Pi)	

Glucose 6-phosphate	-3.4
Glycerol 3-phosphate	-3.3
	-2.2

A perusal of Table 1 indicates that when ADP is hydrolyzed to AMP and inorganic phosphate, the $\Delta G^{o'}$ value of this reaction is the same as that of the reaction, ATP→ADP + Pi, that is -7.3 Kcal/mol. Thus, the two terminals phosphate groups of ATP (β and γ) are both high-energy groups. On the contrary, the $\Delta G^{o'}$ value of hydrolysis of AMP to yield adenosine and phosphate is much lower, that is only -3.4 Kcal/mol. Thus, the phosphate group of AMP (i.e., α-phosphate group of ATP) is in the low energy class. The hydrolysis of ATP to yield AMP plus PPi proceeds with $\Delta G^{o'}$ -7.7 Kcal/mol slightly greater than the $\Delta G^{o'}$ for the hydrolysis of the terminal **γ** phosphate bond.

$$\mathrm{ATP} + \mathrm{H_2O} \longrightarrow \mathrm{AMP} + \mathrm{PPi}$$

The inorganic phosphate is subsequently hydrolyzed by the enzyme pyrophosphatase to yield 2 moles of inorganic orthophosphate. The $\Delta G^{o'}$ the value of this reaction is -6.9 Kcal/mol.

$$\mathrm{PPi} + \mathrm{H_2O} \longrightarrow 2\mathrm{Pi}$$

The overall reaction has a $\Delta G^{o'}$ value -14.6 Kcal/mol which is the sum of the $\Delta G^{o'}$ values of the sequential component reactions.

$$\mathrm{ATP} + \mathrm{H_2O} \longrightarrow \mathrm{AMP} + 2\mathrm{Pi}$$

It is noteworthy that the $\Delta G^{o'}$ of the overall reaction is exactly twice the $\Delta G^{o'}$ of the terminal phosphate groups of ATP and ADP.

Some biosynthetic reactions are, however, driven by nucleotides that are analogous to ATP, namely guanosine triphosphate (GTP), cytidine triphosphate (CTP) are uridine triphosphate (UTP). They are present in all cells but in much lower concentration than ATP. Also found in the cells in low concentrations are the corresponding deoxyribonucleoside 5'-triphosphates denoted as dATP, dGTP, dCTP and dTTP. Although ATP is the mainstream carrier of phosphate groups in the cell, the other types of nucleotides serve certain specific biosynthetic pathways. They acquire their terminal phosphate groups mainly from ATP in reaction catalyzed by MG^{2+} - dependent enzyme called nucleoside diphosphokinases. These enzymes promote the following types of reversible reactions:

$$\mathrm{ATP + GDP \rightleftharpoons ADP + GTP}$$

$$\mathrm{ATP + CDP \rightleftharpoons ADP + CTP}$$

$$\mathrm{ATP + UDP \rightleftharpoons ADP + UTP}$$

$$\mathrm{GTP + UDP \rightleftharpoons GDP + UTP}$$

$$\mathrm{ATP + dCDP \rightleftharpoons ADP + dCTP}$$

The energy contained in ATP may be channelized into different biosynthetic pathways via different nucleoside and deoxynucleoside triphosphates (refer fig.6) biosynthetic products.

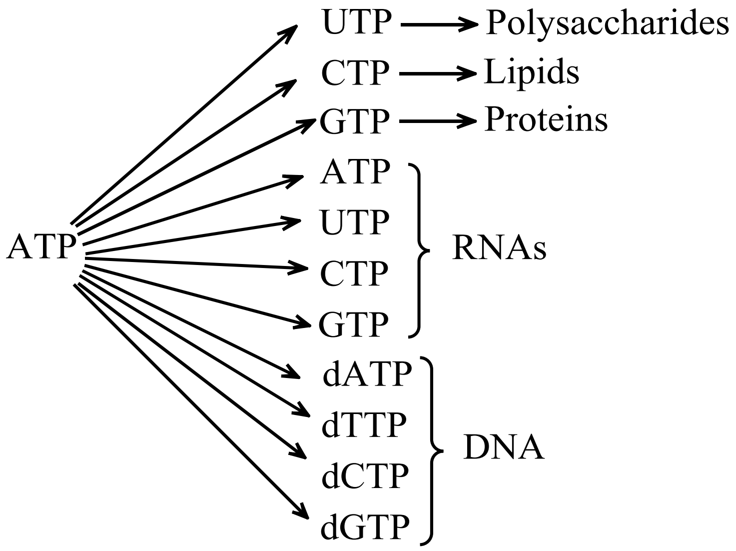


Fig.6 Channeling of ATP energy into various biosynthetic pathways.

6.6 Glycolysis

Carbohydrates are the first cellular constituent formed by photosynthetic organisms and result from the fixation of CO_2 on absorption of light it. The carbohydrates are metabolized to yield a vast array of other organic compounds, many of which are subsequently utilized as dietary constituents by animals. The animals ingest great quantities of carbohydrates that can be either stored, or oxidizing to obtain energy as ATP, or converted to lipids for more efficient energy storage or used for the synthesis of many cellular constituents.

The major function of carbohydrates in metabolism is a fuel to be oxidized and provide energy for other metabolic processes. The carbohydrate is utilized by cells mainly as glucose. The three principle monosaccharide's resulting from digestive processes are glucose, fructose and galactose. Much of the glucose is derived from starch which accounts for over half of the fuel in the diet of most humans. Glucose is also produced from other dietary components by the liver and, to a lesser extent, by the kidneys. Fructose results on large intake of sucrose while galactose is produced when lactose is the principle carbohydrate of the diet.

Both Fructose and galactose are easily converted to glucose by the liver. It is thus apparent that glucose is the major fuel of most organisms and that it can be quickly metabolized from glycogen stores when there arises a sudden need for energy.

Pentose sugars such as arabinose, ribose and xylose may be present in the diet. But their fate after absorption is, however, obscure.

General consideration of glycolysis

Glycolysis (glycos^{G} = sugar (sweet); lysis^{G} = dissolution) is the sequence of 10 enzyme-catalyzed reactions that converts glucose into pyruvate with the simultaneous production of ATP. Moreover, glycolysis also includes the formation of lactate from pyruvate. The glycolytic sequence of reactions from one species to the other only in the mechanism of its regulation and in the subsequent metabolic fate of the pyruvate formed. In aerobic organisms, glycolysis is the prelude to the citric acid cycle and the electron transport chain which together harvest most of the energy contained in glucose. In fact, glycolysis is the central pathway of glucose catabolism. There are three important routes taken by pyruvate after glycolysis, depending on the organism and the metabolic conditions (refer Fig.1.).

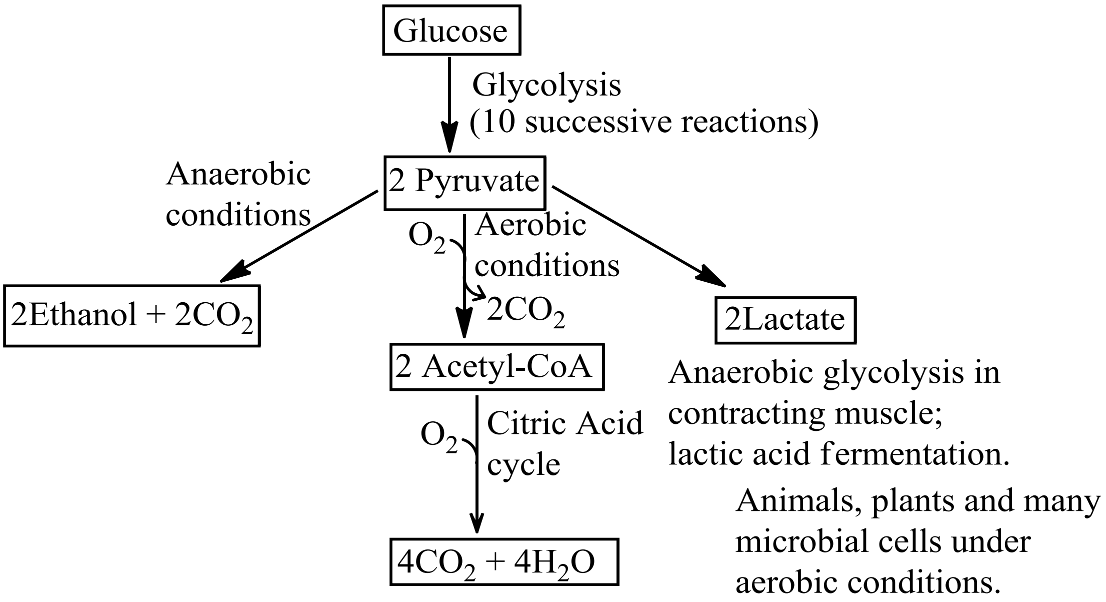


Fig.1-Some important fates of glucose.

a. In aerobic organisms, the pyruvate so formed then enters mitochondria where it is oxidised, with the loss of its carboxyl group as CO_2, to form the style group of acetyl-coenzyme A. Later, the acetyl group is completely oxidised to CO_2 and H_2O to by the citric acid cycle with the intervention of molecular oxygen. This pathway is followed by aerobic animal and plants cells.

b. If the supply of oxygen is insufficient, as in vigorously contracting skeletal muscles, the pyruvate cannot be oxidised further for a lack of oxygen. Under such conditions, it is then reduced to lactate, a process called anaerobic glycolysis. Lactate is also produced from glucose in anaerobic microorganisms that carries out lactic acid fermentation.

c. In some microorganisms (e.g., brewer's yeast), the pyruvate formed from glucose is transformed anaerobically into ethanol and CO_2, a process called alcoholic fermentation. Since living organism first arose in an atmosphere devoid of oxygen, anaerobic breakdown of glucose is the most ancient type of biological mechanism for obtaining energy from organic fuel molecules (Lehninger AL, 1984).

Two phases of glycolysis:-

During glycolysis, the 6 carbon glucose is broken down into two moles of 3-carbon pyruvate via 10 enzyme-catalyzed sequential reactions. These reactions are grouped under two phases, Phase I and II (refer Fig.2)

A. **Phase I or preparatory phase:** It consists of the first five steps. In these reactions, glucose is enzymatically phosphorylated by ATP (first at carbon 6 and later at carbon 1) to yield fructose 1, 6-diphosphate which is then split in half to yield 2 moles of the 3-carbon compound, glyceraldehyde 3-phosphate. The first phase of glycolysis, thus, results in cleavage of the hexose chain.

This phase requires an investment of 2 ATP moles to activate (or prime) the glucose mole and prepare it for its cleavage into two 3-carbon pieces. Besides glucose, other hexoses such as D-fructose, D-galactose and D-mannose may also convert into glyceraldehyde 3-phosphate.

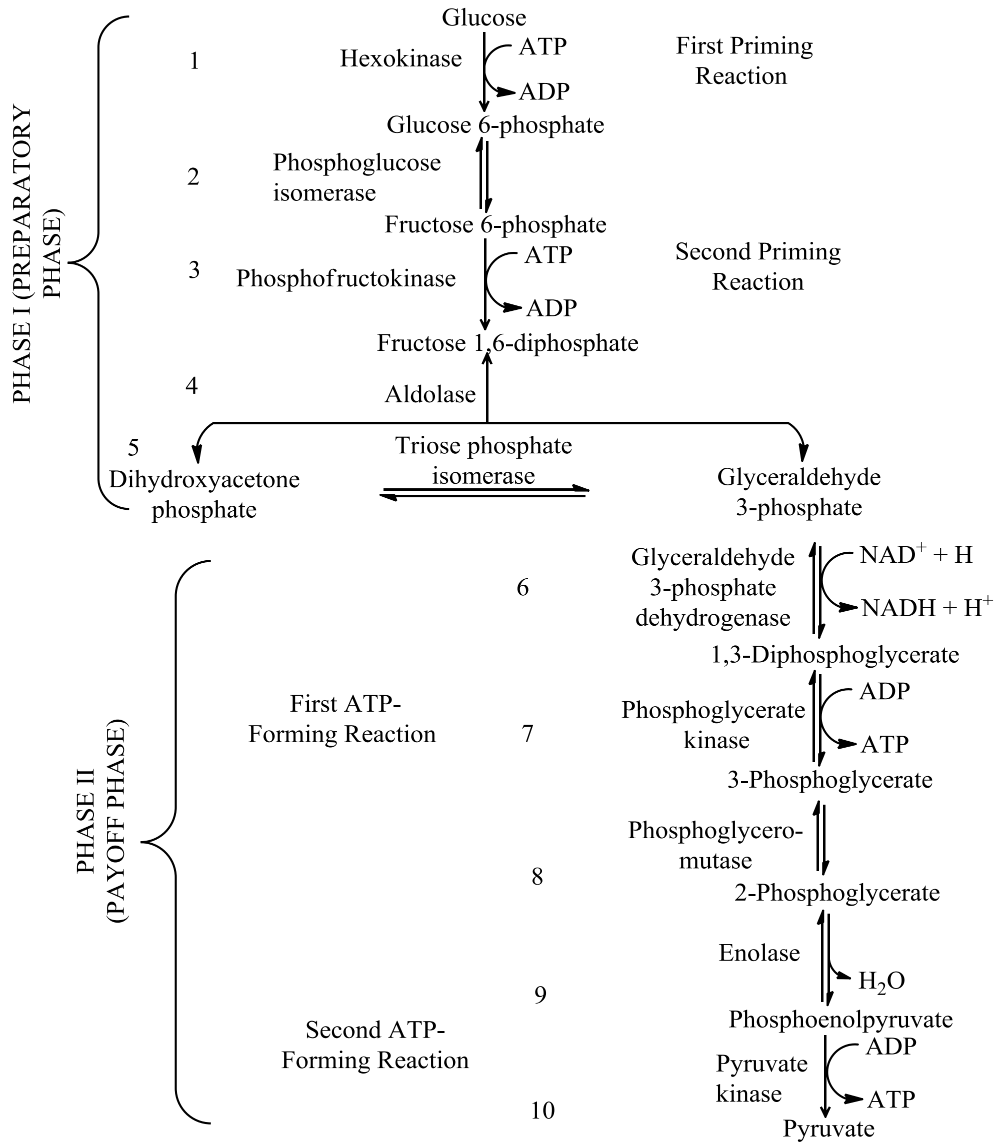


Fig.2 - Two phases of glycolysis

B. **Phase II or Payoff Phase:** The last 5 reactions of glycolysis constitute this phase. This phase represents the payoff of glycolysis, in which the energy liberated during conversion of three moles of glyceraldehyde 3-phosphate 2 moles of pyruvate is converted by the coupled phosphorylation of 4 moles of ADP to ATP. Although 4 moles of ATP are formed in Phase II, the net overall yield is only 2 moles of ATP per mole of glucose oxidized, since 2 moles of ATP are invested in Phase I. The phase II is, thus, energy conserving.

A noticeable feature of glycolysis is that each of the 9 metabolic intermediates between glucose and pyruvate is a phosphorylated compound. The phosphoryl in these compounds are in either ester or anhydride linkage. The phosphoryl or phosphate groups perform following three functions:

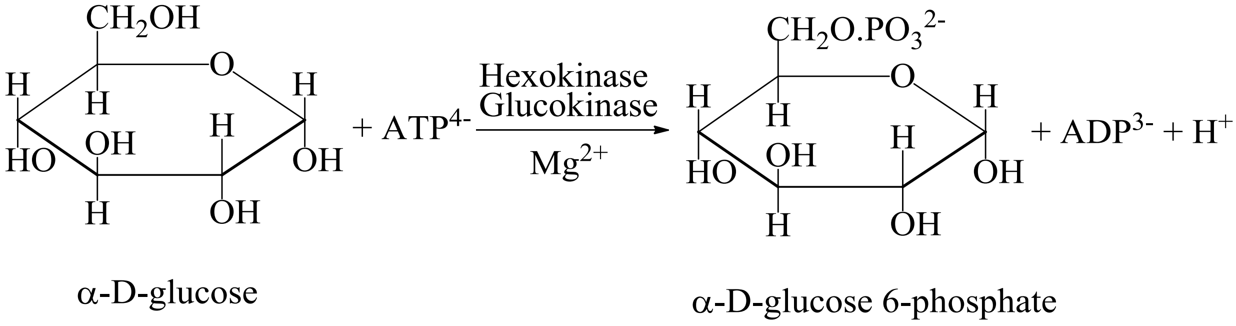
1. The phosphate groups are completely ionized at pH 7, so that each of the nine intermediates of glycolysis gains a net negative charge. Since cell membranes are, in general, impermeable to charged molecules, the glycolytic intermediates cannot escape from the cell. Only glucose can enter cells and pyruvate or lactate can leave cells because cell membranes have specific transport systems that allow these molecules to pass.
2. The phosphate groups are essential components in the conservation of energy since they are ultimately transferred to ADP to produce ATP.
3. The phosphate groups act as recognition for binding groups required for the proper fit of the glycolytic intermediates to the active site of their corresponding enzymes.

Reaction steps of glycolysis

The various reaction steps of glycolysis are schematically represented in Fig.2. The details of these reactions and those of the enzymes, which catalyze them, are given below:

Step-1: Phosphorylation of Glucose-

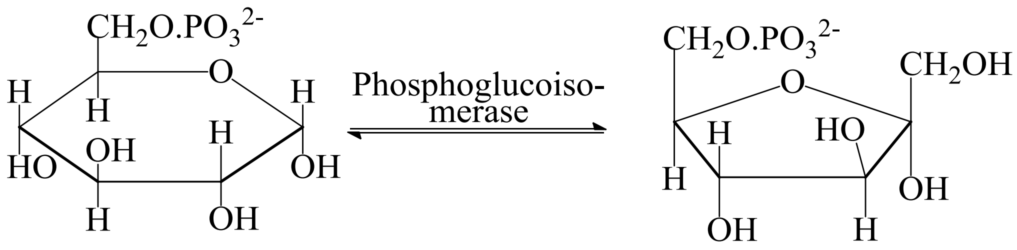
In the first step, glucose is activated (or primed) for subsequent reactions by its phosphorylation at C_6 to yield glucose 6-phosphate, using ATP as phosphate donor. It is phosphoryl transfer type of reaction and is catalysed by the inducible enzyme hexokinase, found in most animal, plants and microbial cells, and by an additional enzyme in the liver, glucokinase. The reaction is accompanied by considerable loss of free energy as heat. It is physiologically irreversible reaction because of the relatively energy character of glucose 6-phosphate and lower stability of MG^{2+}. ADP compared to MG^{2+} ATP. Glucose 6-phosphate it an important compound, being at the junction of many metabolic pathways such as glycolysis, glycogenolysis, gluconeogenesis and the hexose monophosphate shunt.



★ The terms used for glyceric acid, pyruvic acid and lactic acid are respectively, glycerate, pyruvate and lactate. These terms are used to emphasize that at pH of the cell, the acid involved in the reaction is largely in dissociated form.

Step -2: Isomerisation of glucose 6-phosphate-

Glucose 6-phosphate is reversibly isomerized to fructose 6-phosphate by phosphoglucoisomerase. Thus, the 6-membered pyranose ring of glucose 6-phosphate is converted into the 5-membered furanose ring of fructose 6-phosphate. This reaction involves a shift in the carbon and oxygen from C_1 to C_2, thus converting an aldose into a ketose. At equilibrium, the ratio of aldose to ketose is 7:3, i.e. glucose 6-phosphate predominates, having concentration over twice that of fructose 6-phosphate. The reaction proceeds readily in either direction because of relatively small standard free energy change. Fructose 6-phosphate has metabolic fates other than glycolysis.

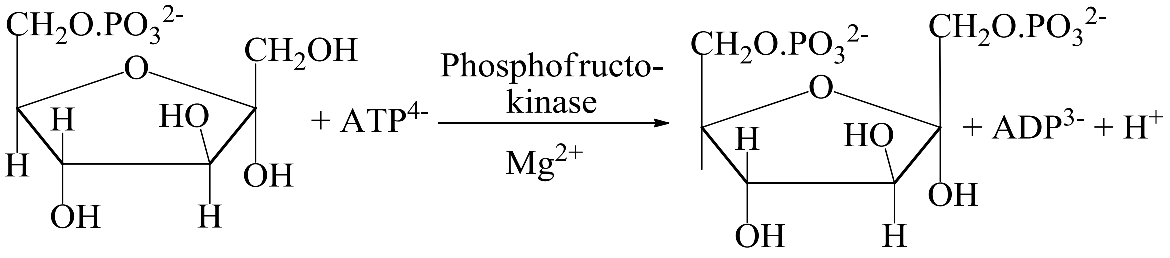


α-D-glucose 6-phosphate
(Robinson's ester)

α-D-fructose 6-phosphate
(Newberg's ester)

Step-3: Phosphorylation of fructose 6-phosphate-

This is the second of two priming for activating reactions of glycolysis (the first one being step 1). Fructose 6-phosphate is phosphorylated by ATP to produce fructose 1, 6-diphosphate in the presence of another inducible enzyme, phosphofructokinase (abbreviated as PFK). The enzyme catalyzes the transfer of a phosphate group from ATP to fructose 6-phosphate at C_1 to yield Fructose 1, 6-diphosphate. Since the reaction proceeds with $\Delta G^{o'}$ = -3.4 KCal/mol, it is essentially irreversible. it is considered to be the committed step in glycolysis since the PFK action 'commits' the cell to metabolizing glucose rather than storing or converting it to some other hexose. In addition to being a key step, it is an important control point of glycolysis.



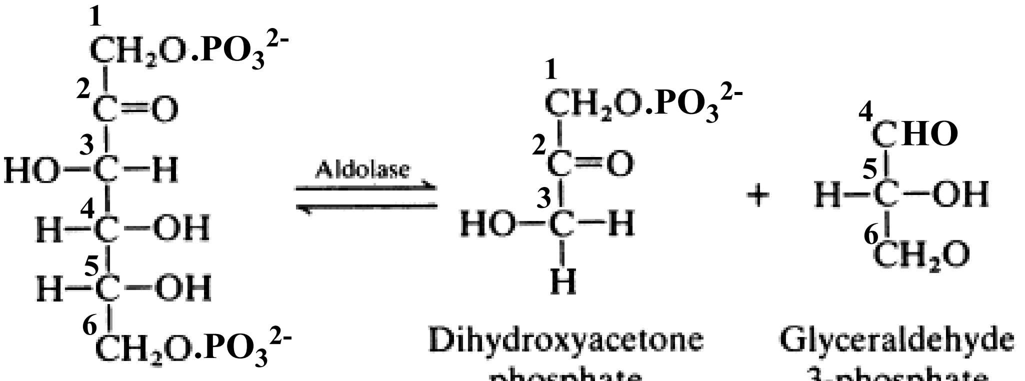
α-D-fructose 6-phosphate
(Newberg's ester)

D-fructose 6-diphosphate
(Harden-Young's ester)

Step-4: Cleavage of fructose 1, 6-diphosphate-

This is a unique C—C bond scission reaction. Since fructose 1, 6- diphosphate is a molecule with phosphate group on both ends; it splits in the middle into two different triose phosphates, glyceraldehyde 3-phosphate (an aldose) and dihydroxyacetone phosphate (a ketone). This reaction is catalyzed by the enzyme fructose diphosphate aldolase (often simply called aldolase) which cleaves the fructose 1,6- diphosphate molecule between C_3 and C_4. Carbon atoms 4, 5 and 6 appear in glyceraldehyde 3-phosphate and 1, 2 and 3 in dihydroxyacetone phosphate. Although the aldose reaction has a highly positive standard free energy change, it readily proceeds in either direction under the pH and concentration conditions existing in cells.

Thus, this is a reversible condensation type of reaction. The remaining steps in glycolysis involve 3 carbon units, rather than 6 carbon units.



Dihydroxyacetone
phosphate

Glyceraldehyde
3-phosphate

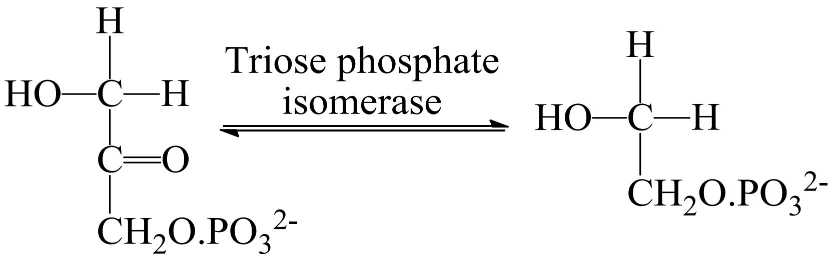
D-Fructose
1,6-bisphosphate

Step-5: Isomerisation of dihydroxyacetone phosphate-

Glyceraldehyde 3-phosphate (an aldose) can be directly degraded in the subsequent reaction steps of glycolysis but dihydroxyacetone phosphate (a ketose) cannot be. However, dihydroxyacetone phosphate can be readily and reversibly converted into glyceraldehyde 3-phosphate by the enzyme triose phosphate are interconverted buy phosphoglucoisomerase.

This is an isomerisation reaction and occurs very rapidly. At equilibrium, about 95% of the triose phosphate it is dihydroxyacetone phosphate.

However, the reaction proceeds towards glyceraldehyde 3-phosphate formation because of the efficient removal of this product. It may be noted that by this reaction, carbon atoms 1, 2 and 3 of the starting glucose now become indistinguishable from carbon atoms 6, 5 and 4 respectively. This reaction completes the first phase of glycolysis.



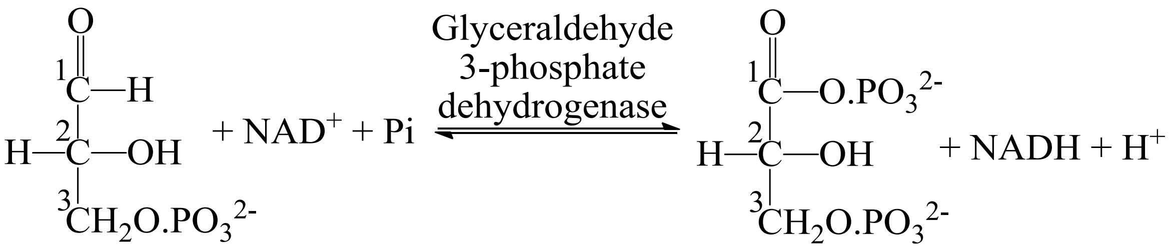
Dihydroxyacetone phosphate (DHA-P)

D-glyceraldehyde 3-phosphate (G3-P)

Step-6: Oxidative phosphorylation of glyceraldehyde 3 phosphate

This is first of the two energy-conservation reactions of glycolysis (the second one being step 9) in which a high energy phosphate compound, 3-phosphoglycerol phosphate is formed. Here, glyceraldehyde 3-phosphate is converted into 3-phosphoglycerol phosphate (=1, 3-diphosphoglycerate, 1, 3-DPG) by the enzyme glyceraldehyde 3-phosphate dehydrogenase (= phosphoglyceraldehyde dehydrogenase), which is NAN^+ dependant.

In this complex and reversible reaction, the aldehyde group of glyceraldehyde 3-phosphate dehydrogenated, not to a free carboxyl group, but to a carboxylic anhydride with phosphoric acid, the 3-phosphoglycerol phosphate. This type of anhydride called an acyl as phosphate has a very high standard free energy or hydrolysis ($\Delta G^{o'}$ = -11.8 KCal/mol) and is thus a super high energy phosphate (refer table). The acyl phosphate or 1, 3-diphosphoglyceraldehyde conserves much of the free energy liberated during oxidation of the aldehyde group of glyceraldehyde 3-phosphate. A value of ($\Delta G^{o'}$) for this reaction is +1.5 KCal/mol.

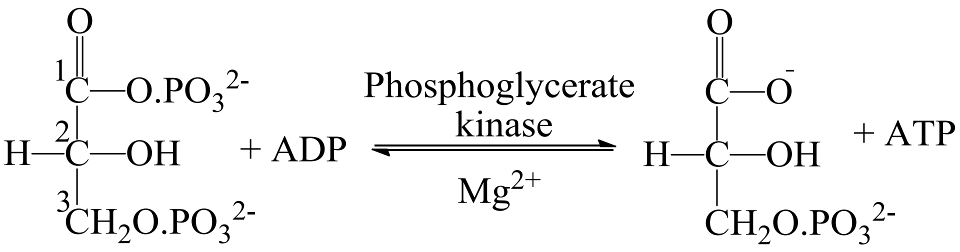


D-glyceraldehyde 3-phosphate (G3-P)

3-phosphoglycerol phosphate

Step-7: Transfer of phosphate from 1, 3-DPG to ADP-

This is the first ATP generating reaction in glycolysis (the second one being step 10) it involves the transfer of high energy phosphate group from the carboxylic group 3 phosphoglycerol phosphate (=1, 3- phosphoglycerate or 1, 3- DPG) to ADP but the enzyme phosphoglycerate kinase, thus producing ATP and leaving 3-phosphoglycerate. Since 2 moles of triose phosphate are produced per mole of glucose, 2 moles of ATP are generated at this stage per mole of glucose is oxidized. The value of $\Delta G^{o'}$ for this essentially reversible reaction is -4.5 KCal/mol.



1,3-diphosphoglycerate

3-phosphoglycerate

The metal interacts with the ADP to form the reactive complex. This and the preceding reaction (i.e. Steps 6 and 7) together constitute an energy coupling process. The sum of these two sequential reactions would give:

Glyceraldehyde 3-phosphate + NAN$^+$ + Pi + ADP

$\rightleftharpoons$ 3-phosphoglycerate + ATP + NADH + H$^+$

$$\Delta G^{o'} = (+1.5) + (-4.5)$$

$$= -3.0 \text{ KCal/mol}$$

Thus, the net outcome of steps 6 and 7 is:

a. Glyceraldehyde 3-phosphate, and aldehyde, is oxidized to 3-phosphoglycerate, a carboxylic acid.

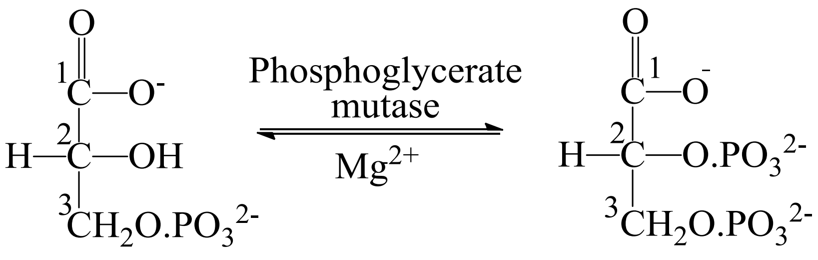
b. NAD$^+$ is reduced to NADH.

c. ATP is produced from ADP and Pi.

In other words, the net result of steps 6 and 7 is that the energy released on oxidation (or dehydrogenation) of an aldehyde to a carboxylate group is conserved by the coupled formation of ATP from ADP and Pi. Such reactions are called substrate level phosphorylation because the energy required to bring them about arises from the dehydrogenation of an organic substrate molecule (for example, glyceraldehyde 3-phosphate in the present case). This term distinguishes this phosphorylation from oxidative phosphorylation, which is the formation of ATP coupled to the oxidation of NADH and FADH$_2$ by oxygen. As the oxidative phosphorylation is coupled to electron transport, it is also called as respiratory-chain phosphorylation.

Step-8: Isomerisation of 3-phosphoglycerate-

3-phosphoglycerate is converted into 2-phosphoglycerate due to the intermolecular shift of phosphorus group from C$_3$ to C$_2$ by the enzyme phosphoglycerate mutase (= phosphoglyceromutase). This is reversible with a $\Delta G^{o'}$ value = +1.06 KCal/mol.

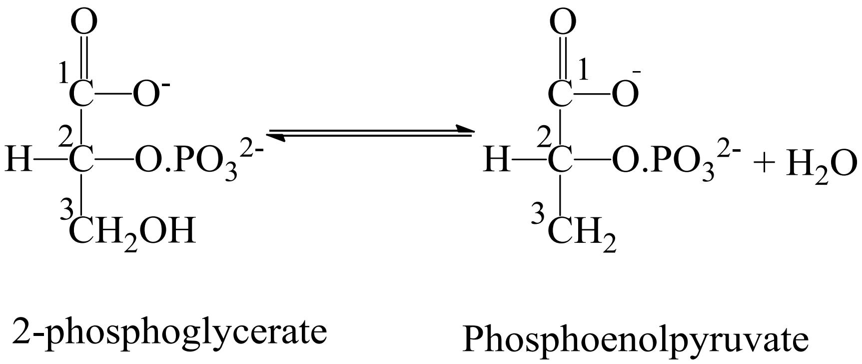


3-phosphoglycerate

2-phosphoglycerate

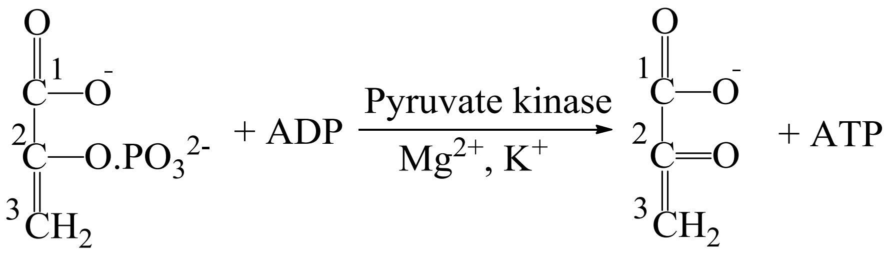
Step-9: Dehydration of 2-phosphoglycerate-

This is the second reaction of glycolysis in which a high-energy phosphate compound (i.e; phosphopyruvate hydratase) to phosphoenolpyruvate (abbreviated as PEP), which is the phosphate ester of enol tautomer of pyruvate. This is a reversible reaction and has a relatively small free energy change value of +0.44 KCal/mol. At equilibrium, the ratio of 2-phosphoglycerate, to phosphoenolpyruvate is 2:1.However, phosphoenolpyruvate, and not 2-phosphoglycerate, contains a sugar high energy phosphate bond. The loss of water from 2-phosphoglycerate causes a redistribution of energy within the molecule, raising the phosphate on position 2 to the high energy state, thus forming PEP. The reaction is freely reversible since there is little free energy change. The $\Delta G^{o'}$ value for the hydrolysis of PEP is -14.8 KCal/mol. There is more than sufficient energy to allow synthesis of ATP from PEP in the next step of glycolysis.



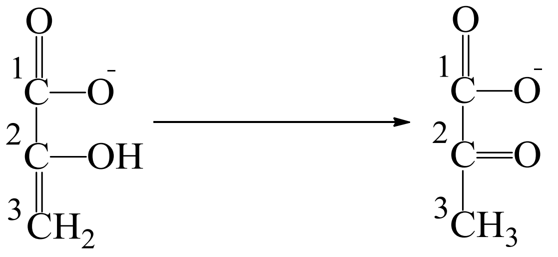
Step-10: Transfer of phosphate from PEP to ADP-

This is the second ATP generating reaction in glycolysis. Here, phosphoenolpyruvate (PEP) is converted into pyruvate in enol form (i.e, enolpyruvate) by the inducible allosteric enzyme pyruvate kinase (abbreviated as PK). The enzyme catalyzes the transfer of a phosphoryl group from PEP to ADP, thus forming. This phosphorylation reaction is non oxidative in contrast with the one catalyzed by glyceraldehyde 3-phosphate dehydrogenase (i.e, step 6). This is another physiologically irreversible step in glycolysis (the first one being step 1) and proceeds with $\Delta G^{o'} = -7.5$ KCal/mol.



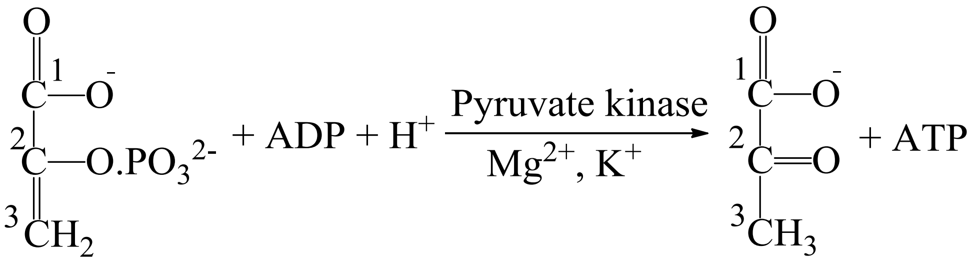
Phosphoenolpyruvate Enolpyruvate

The enolpyruvate, however, rearrange is rapidly and monenzymatically to yield the keto form of pyruvate (i.e, ketopyruvate). The keto form predominates at pH 7.0.



Enolpyruvate Ketopyruvate

The point of equilibrium of this non-enzymatic reaction is very far to the right. Therefore it ‘drives’ the preceding enzymatic to the right by mass action. The two reactions, on addition, give:



Phosphoenol pyruvate Ketopyruvate

The overall reaction has a very large negative $\Delta G^{o'}$ value due to the spontaneous conversion of enol form of pyruvate to the keto form. The $\Delta G^{o'}$ value for hydrolysis of PEP is -14.8 KCal/mol. About half of this energy is recovered as ATP ($\Delta G^{o'}$ = -7.3KCal/mol) and the rest (-7.5 KCal/mol) constitutes a large driving force, pushing the reaction far to the right. Since 2 moles of PEP are formed per mole of glucose oxidized, 2 moles of ATP are also produced per mole of glucose. The conversion of phosphoenolpyruvate into pyruvate is the second example of substrate level phosphorylation in glycolysis.

In metabolic pathways, the enzymes catalyzing essentially reactions are the key sites of control. In glycolysis, the steps 1, 3 and 10 which are catalyzed by hexokinase (or glucokinase), phosphofructokinase and pyruvate kinase respectively are virtually irreversible. Hence, they perform regulatory as well as catalytic functions.

Stoichiometry of glycolysis

Overall balance sheet

Keeping in mind that each molecule of glucose yield 2 molecules of glyceraldehyde 3-phosphate, the total inputs and outputs of all the 10 glycolysis may be written as follows:

$$\text{Glucose} + 2\text{ATP} + 2\text{Pi} + 2\text{NAD}^+ + 4\text{ADP} \longrightarrow$$
$$2\text{Pyruvate} + 2\text{H}^+ + 4\text{ATP} + 2\text{H}_2\text{O} + 2\text{NADH} + 2\text{H}^+ + 2\text{ADP}$$

On cancelling the common terms, we get net equation for the transformation of glucose into pyruvate:

$$\text{Glucose} + 2\text{ATP} + 2\text{Pi} + 2\text{NAD}^+ + 4\text{ADP} \longrightarrow$$
$$2\text{Pyruvate} + 2\text{ATP} + 2\text{H}_2\text{O} + 2\text{NADH} + 2\text{H}^+$$

Thus, three things happen simultaneously in glycolysis:

a. Glucose is oxidised to pyruvate

b. NAD^+ is reduced to NADH.

c. ADP is phosphorylated to form ATP.

There can be no EMP pathway without all 3 events which means that NAD^+, ADP and Pi, as well as glucose, must be present.

Energy Yield

Further, 2 moles of ATP are generated in glycolysis. A summary of the steps in which ATP is consumed are formed is given in Table 2.

Table-2: Energy yield of glycolysis

Step	Reaction	Consumption of	Gain of

		ATP	ATP
1.	Glucose → Glucose 6-phosphate	1	
2.	Fructose 6-phosphate → Fructose 1, 6-diphosphate	1	
3.	1,3-diphosphoglycerate → 3-phosphoglycerate		1 x 2 = 2
10.	Phosphoenolpyruvate → Pyruvate		1 x 2 = 2
		2	4
Net gain of ATP = 4-2 = 2			

6.7 Summary

Carbohydrates occupying an important place in metabolism as they are a major source of energy for living organisms. In our food, the chief source of carbohydrate is starch; they are polysaccharides produced by plants especially the cereal crops during photosynthesis. Plant starch is also the main source of energy for domestic and wild animals. Relatively e large amounts of starch can be stored in plant cells in times of abundant supply and which is used when there is a demand for energy production. The hydrolysis of starch is catalyzed by enzymes known as amylase which occurs in saliva and the pancreatic juice. The analysis of animal origin is called α-amylase in order to distinguish them from α-amylase of plant. This differ in their point of attack on the starch molecule are the α-amylases are exoamylase and catalyze maltose units from the end of amylase where as α-amylase are enko amylases and catalyze the breakdown of bonds occurring in the interior of the molecules. The first products of the action of the α-amylase are the dextrins which are progressively degraded into two smaller and smaller units. Apart from starch, cellulose is also produced by plants in large amounts as a structural carbohydrate.

Glucose breakdown:

Glucose is used both by aerobic and anaerobic organisms. There are three integrated pathways which are responsible for the breakdown of glucose and its conversion to CO_2, water and utilizable energy. These are-

1. The glycolysis of embden meyrhot pathway.
2. The citrate cycle and electron transport chain.
3. The pentose phosphate pathway.

Glycolysis:

The meaning of glycolysis is sugar splitting. The end result is the splitting of one molecules of glucose phosphate into two molecules of pyruvic acid with the production of ATP. In the initial stages this pathway is the same in aerobic and anaerobic organisms.

Adenosine triphosphate (ATP)

ATP acts as a carrier of chemical energy from energy releasing to energy requiring processes in the cell. That is why it is called the energy currency of the cells. It is a nucleotide containing at adenine as the nitrogen base, ribose as the sugar of three interlinked phosphate units.

In the presence of suitable catalyst, ATP undergoes hydrolysis of the three P—O bond is three steps. In the first step, ATP is hydrolysed to ADP with the release of 31 KJ/mole Gibbs energy. In the second step ADP is converted into AMP (adenosine monophosphate) and produces approx the same (i.e. 31 KJ/mol) amount of energy. In the last step of hydrolysis of AMP to adinosine only for only 14 KJ/mol

Gibbs energy is released.

Thus, conversion of ATP to ADP is highly exergonic $\Delta G^{o'} = -31.0\ KJmol^{-1}$ and hence can drive any thermodynamically forbidden reaction into to the desired direction. This normally happens in several metabolic process in the body.

Carbohydrate metabolism:

In cells, glucose is oxidised to CO_2 and H_2O in a number of enzyme catalyzed reaction. This energy released during catabolism of glucose is used for synthesis of ATP. The oxidation of glucose takes place in two stages:-

1. Glycolysis is the first stage in the oxidation of glucose it is an anaerobic process and involves the degradation of glucose into two molecules of pyruvate with the generation of two molecules of ATP
2. Cellular respiration is the second stage in the oxidation of glucose. It is an aerobic process and involve the oxidation of pyruvate to CO_2 and H_2O. During the complex oxidation of each molecule of glucose, 38 molecules of ATP are produced.

6.7. Terminal questions

1. How can you say that ATP is the currency of energy?
2. What is application of bioenergetics to the living system?
3. How Gibbs free energy is related to the biological system?
4. Give the pathway for glycolysis.
5. Discuss briefly the sequence of reactions involved in glycolysis.
6. Explain the function of structure of ATP
7. What do you know about metabolic routes?
8. Explain the term glycolysis.
9. How glycolysis is different from fermentation?