PHOTOCHEMISTRY: STUDY MATERIAL AND NUMERICAL PROBLEMS

INTRODUCTION TO PHOTOCHEMISTRY AND ELECTROMAGNETIC RADIATION

Photochemistry is the study of chemical reactions initiated by the absorption of light. The energy from photons causes molecules to reach excited states, from which they can undergo chemical transformations.

Characteristics of Electromagnetic Radiation:

- **Wavelength (λ):** The distance between successive crests of a wave. Units: meters (m), nanometers (nm), angstroms (Å).
- **Frequency (ν):** The number of wave cycles passing a point per unit time. Units: Hertz (Hz) or s^{-1}.
- **Wavenumber ($\bar{\nu}$):** The reciprocal of wavelength. Units: cm^{-1} or m^{-1}.
- **Energy (E):** The energy of a photon is directly proportional to its frequency, as given by Planck's equation: $\mathbf{E = h\nu}$, where 'h' is Planck's constant (6.626×10^{-34} J·s). Since $\nu = c/\lambda$ (where c is the speed of light), energy can also be expressed as $\mathbf{E = hc/\lambda}$.

LAMBERT-BEER’S LAW AND ITS LIMITATIONS

Lambert-Beer’s Law describes the absorption of light by a substance in solution. It relates the absorbance of a solution to the properties of the solute and the path length of the light beam through the solution.

The Law: $A = \varepsilon bc$

- **A**: Absorbance (dimensionless).
- **ε**: Molar absorptivity (or extinction coefficient). It is a measure of how strongly a chemical species absorbs light at a given wavelength. Units: L mol^{-1} cm^{-1}.
- **b**: Path length of the light beam through the sample. Units: cm.
- **c**: Concentration of the absorbing species. Units: mol L^{-1}.

Physical Significance of Absorption Coefficients:

Molar absorptivity (ε) indicates the efficiency of light absorption by a specific molecule at a particular wavelength. A higher ε means the substance absorbs light more strongly per unit concentration and path length.

Limitations of Lambert-Beer's Law:

- The law is strictly valid only for dilute solutions. At high concentrations, intermolecular interactions can alter the molar absorptivity.
- It assumes monochromatic light. If polychromatic light is used, the absorptivity can vary for different wavelengths, leading to deviations.
- The absorbing species must be homogeneous and not undergo chemical changes (e.g., association, dissociation, or reaction with the solvent) during measurement.
- The presence of scattering by particles in the solution can cause apparent deviations.

LAWS OF PHOTOCHEMISTRY

1. Stark-Einstein Law of Photochemical Equivalence:

This fundamental law states that for every photon of light absorbed by a molecule, exactly one molecule undergoes a primary photochemical process (e.g., excitation, dissociation, ionization). The number of molecules reacting in the primary step is equal to the number of photons absorbed.

2. Quantum Yield (Φ):

The quantum yield is a measure of the efficiency of a photochemical process. It is defined as the ratio of the number of molecules undergoing a specific process (e.g., reactant consumed, product formed, photon emitted) to the number of photons absorbed by the system.

Φ = (Number of moles of reactant consumed or product formed) / (Number of moles of photons absorbed)

- Low Quantum Yields: Occur when absorbed energy is lost through non-productive pathways, such as fluorescence, phosphorescence, internal conversion, or when the excited state quickly reverts to the ground state via reverse reactions or recombination before it can react.

- High Quantum Yields: Indicate that one absorbed photon leads to the formation or consumption of many molecules. This typically happens in chain reactions where the absorbed photon initiates a chain-initiating step, and subsequent chain propagation steps consume or form many molecules.

Actinometry:

Actinometry is the technique used to measure the intensity of light or the radiant energy incident on a system. It involves using a chemical system (an actinometer) whose quantum yield is precisely known under specific conditions. By measuring the extent of the chemical change in the actinometer and knowing its quantum yield and the duration of irradiation, the number of photons absorbed can be calculated.

A common example is the Potassium Ferrioxalate actinometer.

RATE OF PHOTOCHEMICAL PROCESSES AND PHOTO-STATIONARY STATE

Photochemical reactions proceed at rates determined by the rate of light absorption and the quantum yield. The differential rate equation often depends on the intensity of incident light, the concentration of reactants, and the quantum yield.

Photo-stationary State:

In a reversible photochemical reaction, a photo-stationary state is reached when the rate of the forward photochemical reaction becomes equal to the rate of the reverse thermal reaction (or the reverse photochemical reaction). This state is maintained as long as the system is irradiated, and it is different from thermodynamic equilibrium because it depends on the intensity and wavelength of light.

EXAMPLES OF PHOTOCHEMICAL REACTIONS

1. HI Decomposition:

The photolysis of hydrogen iodide in the gas phase:

$2HI(g) + h\nu \rightarrow H_2(g) + I_2(g)$

This reaction typically has a quantum yield close to 2 under certain conditions, as the absorption of one photon can lead to a chain mechanism.

2. H_2-Br_2 Reaction:

A classic example of a photochemical chain reaction initiated by UV light:

$$H_2(g) + Br_2(g) + h\nu \rightarrow 2HBr(g)$$

This reaction exhibits a very high quantum yield due to its free-radical chain mechanism.

3. Dimerization of Anthracene:

Anthracene can undergo reversible photodimerization in the solid state or in solution upon UV irradiation:

$$2\ \text{Anthracene} + h\nu \rightleftharpoons \text{Anthracene dimer}$$

The quantum yield depends on factors like concentration, phase, and temperature.

PHOTOSENSITIZED REACTIONS AND QUENCHING

Photosensitized Reactions:

In these reactions, a molecule (the sensitizer) absorbs light and then transfers the absorbed energy to another molecule (the reactant), which then undergoes chemical transformation. The sensitizer is regenerated and can initiate the process again.

Quenching:

Quenching refers to the deactivation of an excited state molecule. This can occur through radiative processes (like fluorescence) or non-radiative processes (like collisional deactivation with other molecules). Quenching reduces the lifetime of the excited state and can lower the quantum yield of a photochemical reaction.

Stern-Volmer Equation:

The Stern-Volmer equation relates the fluorescence intensity (or lifetime) of a molecule to the concentration of a quencher (Q). It is widely used to study quenching mechanisms and determine rate constants.

For fluorescence quenching, it is often expressed as:

$$(F_0 / F) = 1 + kq\tau_0[Q]$$

- F_0: Fluorescence intensity in the absence of quencher.
- F: Fluorescence intensity in the presence of quencher.
- kq: The bimolecular quenching rate constant.

- τ_0: The excited state lifetime in the absence of quencher.
- [Q]: The concentration of the quencher.

ROLE OF PHOTOCHEMICAL REACTIONS IN BIOCHEMICAL PROCESSES

Photochemistry plays vital roles in many biological systems:

- **Vision:** The isomerization of retinal in rhodopsin, triggered by light, is the first step in the visual process.
- **Vitamin D Synthesis:** UV light initiates the conversion of 7-dehydrocholesterol in the skin to previtamin D_3.
- **Photosynthesis:** Light energy is captured and converted into chemical energy by plants and other organisms.
- **DNA Damage and Repair:** UV radiation can cause photochemical damage to DNA (e.g., thymine dimers), which cells have repair mechanisms to address.
- **Circadian Rhythms:** Light influences biological clocks through photoreceptors.

NUMERICAL PROBLEMS ON PHOTOCHEMISTRY

Numerical problems in photochemistry typically involve applying the laws and concepts discussed above. You will often be asked to calculate:

- The energy of photons given wavelength or frequency.
- The number of photons absorbed or emitted.
- The concentration of a substance using Lambert-Beer's Law, given absorbance and molar absorptivity.
- The quantum yield of a reaction, given the amount of reactant consumed/product formed and the number of photons absorbed.
- Parameters in the Stern-Volmer equation, given fluorescence intensities at different quencher concentrations.
- Rates of photochemical reactions based on light intensity and quantum yield.

General Approach to Solving Numerical Problems:

1. Identify the given information and what needs to be calculated.
2. Determine which laws or equations are relevant (e.g., $E=h\nu$, $A=\varepsilon bc$, Φ definition, Stern-Volmer equation).
3. Ensure all units are consistent before performing calculations.

4. Break down complex problems into smaller steps.
5. Pay close attention to the definition of quantum yield (moles of photons vs. number of photons, moles of reactant vs. number of molecules).

Example Problem Structure:

Problem Type 1 (Energy Calculation): Calculate the energy of a photon of green light with a wavelength of 550 nm.

Problem Type 2 (Lambert-Beer's Law): A solution of a dye has a molar absorptivity of 50,000 L mol^{-1} cm^{-1} at 450 nm. If a 1 cm cuvette containing the dye solution has an absorbance of 0.75 at 450 nm, what is the concentration of the dye?

Problem Type 3 (Quantum Yield): A photochemical reaction is carried out using monochromatic light of wavelength 300 nm. If 100 J of light energy is absorbed by the sample, and 0.01 moles of product are formed, what is the quantum yield of the reaction?

Problem Type 4 (Stern-Volmer): Fluorescence intensity measurements of a compound show F_0 = 100 units and F = 50 units when the quencher concentration is 0.1 M. If the excited state lifetime τ_0 is 10 ns, calculate the quenching rate constant k_q.