

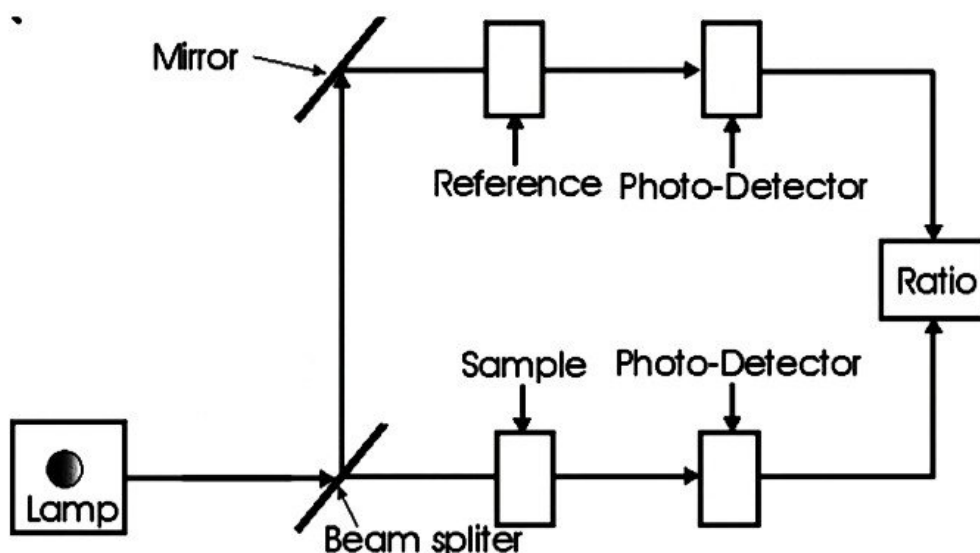
Class Test 1 (CYL1010)

Total marks 10

All questions are mandatory

Q.1 Study the following figure carefully.

A) Select the correct statements: [2]



1. The figure represents spectrophotometer for recording absorption as well as emission spectra of a molecule.
2. The reference chamber contains solvent that does not respond to the wavelength range scanned by the spectrometer.
3. The beam splitter is a half-silvered mirror that is moving with a fixed velocity.
4. The spectrometer design allows polychromatic light to enter the sample.
5. The instrument measures absorbance only without displaying the spectrum of a sample.
6. The photodetector works on the principle of photoelectric effect.

Correct statements: 2, 4, 5, 6 [Each statement carries 0.5 marks]

B) State the laws of absorption applicable for the spectrophotometer. [2]

The Beer-Lamber law is applicable for spectrophotometers. [0.5 mark]

- The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment. [0.5 mark]
- The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette. [0.5 mark]
- $A = \epsilon cl$ where ϵ denotes the molar absorptivity coefficient [0.5 mark]

C) What change will be required in the dimension of sample chamber if we measure gaseous sample in place of liquid? [1]

The length of the sample chamber needs to be increased allowing light to travel through a longer pathlength.

Q.2. Consider a hypothetical situation where the lifetime of an excited electronic state becomes infinitely long. What change will you observe in the spectral appearance and why? [3]

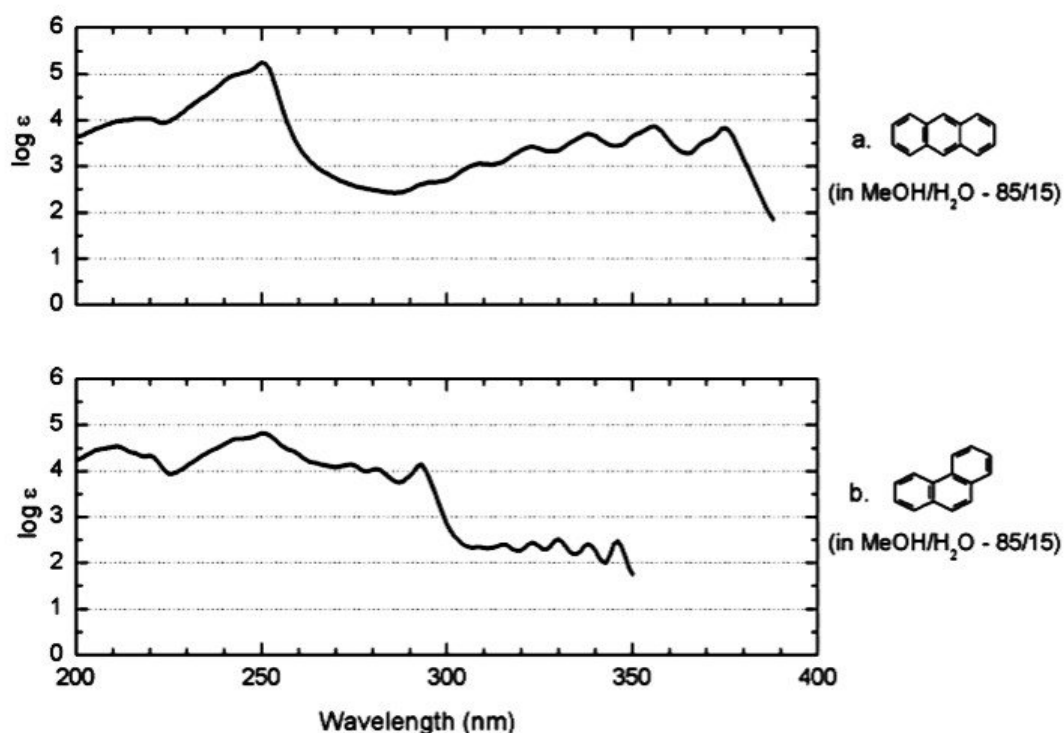
In case the lifetime (τ) of an excited state becomes infinitely long, the spectral line will become infinitely sharp or will look like a 'delta' function. This is due to the inverse relation of lifetime with linewidth of spectral line and is an outcome of Heisenberg uncertainty principle.

$$\Delta E \Delta \tau \leq h/2\pi$$

$$\text{Or } \Delta \nu \Delta \tau \leq 1/2\pi$$

[1 mark for first line and 2 marks for the reasoning]

Q.3. The λ values measured for UV-Vis absorption spectra of Phenanthrene and Anthracene ranges from 200-350 nm and 200-390 nm respectively with Anthracene showing a higher absorption intensity. Justify this observation by examining the following figure. [2]



Both anthracene and phenanthrene are polycyclic aromatic hydrocarbons (PAH). Anthracene is the linear chain PAH while phenanthrene is the angular isomer. Linear chain allows better conjugation of the π -electrons decreasing the HOMO-LUMO gap considerably compared to

the angular isomers. Hence anthracene shows bathochromic (red shift) as well as hyperchromic shifts (higher ϵ) over the entire wavelength range of absorption.

[No partial marking for the above question]

Class Test 2 (CYL1010)

Total marks 10

All questions are mandatory

Q.1 Calculate the amplitude of vibration (extent of v) of CO in its ground vibrational level ($v = 0$), assuming it to be a classical harmonic oscillator. Given the energy of each vibrational level $E_v = (v+1/2)h\nu$; v = vibrational quantum number. The force constant of the bond is $k = 1901 \text{ N m}^{-2}$, the equilibrium bond length is 112.8 pm . [5]

Considering SHO model for the bond vibration we can write

$E = \frac{1}{2} kx^2$ where x = amplitude of vibration. [1 mark]

Given $E_v = (v+1/2)h\nu$ and $v = 0$ (Ground vibrational state)

Hence $(v+1/2)h\nu = \frac{1}{2} kx^2$ [1 mark]

$$\text{Or, } \frac{1}{2} h\nu = \frac{1}{2} kx^2$$

$$\text{Or, } x^2 = \frac{h\nu}{k}$$

$$\text{Or, } x = \sqrt{\frac{h\nu}{k}} \quad [1 \text{ mark}]$$

Now the frequency of vibration can be calculated as $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ where $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ [1 mark]

Now $1 \text{ N} = 1 \text{ kg m s}^{-2} = 1 \text{ J m}^{-1}$, therefore $k = 1901 \text{ kg m s}^{-2} \text{ m}^{-1} = 1901 \text{ kg s}^{-2} = 1901 \text{ J m}^{-2}$

$$\mu = 1.138 \times 10^{-26} \text{ kg}$$

$$x = \sqrt{\frac{6.626 \times 10^{-34}}{1901} \frac{1}{2 \times 3.141}} \sqrt{\frac{1901}{1.138 \times 10^{-26}}} \text{ m} \quad [1 \text{ mark}]$$

Q.2. Select the correct statements about Raman scattering. [2]

- a) Intensity of Raman scattering is more for a liquid compared to a gaseous sample.
- b) The scattered photons are best detected at a 45° angle with the incident beam.
- c) Raman scattering is caused due to absorption of light.
- d) Fluorescence can obscure intensity of Raman scattering.

Statement a) and d) correct [each carry 1 mark]

Q.3. Select the incorrect statements about bond vibration. [2]

- a) Absorption of infrared radiation causes change in vibrational frequency of a bond.
- b) All chemical bond vibrations can be detected by IR but not by Raman spectroscopy.

c) Simple harmonic oscillator is a correct representation of chemical bond vibration.

d) Vibrational transition to a higher energy level can rupture a chemical bond.

b) and c) are incorrect statements. [each carry 1 mark]

Q.4. What is liquid junction potential? [1]

Liquid junction potential is an additional source of potential caused due to ion movement at the interface of two electrolytes. [1 mark]

This can also be created due to concentration gradient across electrolyte interface in an electrolyte concentration cell. This can be removed by using a salt bridge.

Class Test 3 (CYL1010)

Total marks 10

All questions are mandatory

Q.1 The following table gives you the standard reduction potential of some of the half-cell reactions:

$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$	-0.763
$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$	-0.44
$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$	0.000
$\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$	+0.337
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.771
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.7794

- a) Using the above table identify the anode and the cathode and determine the cell potential of a galvanic cell composed of Copper and Iron? [5]

Galvanic cell will have spontaneous chemical reaction. Hence the reaction Gibbs free energy will be negative. Therefore, from the relation $\Delta G = -nFE^\circ$, one could understand that the cell potential should be positive.

$$E^\circ = E_{\text{cathode}} - E_{\text{anode}} = +\text{ve quantity} \quad [\text{This argument carries 2 marks}]$$

Therefore, $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$ +0.337 is the cathode [1 mark]

$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$ -0.44 is the anode. [1 mark]

$$\text{Cell potential } E^\circ = E_{\text{cathode}} - E_{\text{anode}} = 0.337 - (-0.44) = +0.777 \text{ V. [1 Mark]}$$

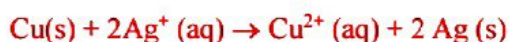
- b) For the cell $\text{Cu (s)} | \text{Cu}^{2+} || \text{Ag}^+ (1\text{M}) | \text{Ag (s)}$ calculate the cell potential and the reaction Gibbs free energy. [5]

Anode: $\text{Cu (s)} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ (oxidation at anode) [1 mark]

Cathode: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag (s)}$ (reduction at cathode) [1 mark]

$$E^\circ = E_{\text{cathode}} - E_{\text{anode}} = 0.7794 - 0.337 = 0.4424 \text{ V} \quad [1 \text{ mark}]$$

The total cell reaction:



Since 2e^- are involved in the process

$$\Delta G = -nFE^\circ = -2(96485 \text{ J V}^{-1} \text{ mole}^{-1})(0.4424 \text{ V}) = -85369.9 \text{ J mole}^{-1} \quad [2 \text{ marks}]$$

Qn 1. (a)

Calculate the maximum kinetic energy of photoelectrons emitted from Na exposed to 260 nm light.

The maximum kinetic energy (E_{kinetic}) of photoelectrons can be calculated using the photoelectric effect equation:

$$\begin{aligned} E_{\text{kinetic}} &= h\nu - \phi \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \cdot (3 \times 10^8 \text{ m/s})}{260 \times 10^{-9} \text{ m}} - (2.75 \text{ eV} \cdot 1.602 \times 10^{-19} \text{ J/eV}) \end{aligned}$$

Thus, the maximum kinetic energy of photoelectrons is $3.2395 \times 10^{-19} \text{ J}$.

Qn 1. (b)

Calculate the longest wavelength that will initiate the photoelectric effect in pure Na.

To find the longest wavelength (λ_{max}) that will initiate the photoelectric effect, we use the work function (ϕ) and the photoelectric effect equation:

$$\lambda_{\text{max}} = \frac{c}{\nu_{\text{max}}}$$

Where ν_{max} is the frequency corresponding to the longest wavelength, and it's when $E_{\text{kinetic}} = 0$. We can calculate ν_{max} as:

$$\nu_{\text{max}} = \frac{\phi}{h}$$

Substituting the values:

$$\nu_{\text{max}} = \frac{2.75 \text{ eV} \cdot 1.602 \times 10^{-19} \text{ J/eV}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}$$

Now, find the longest wavelength:

$$\lambda_{\text{max}} = \frac{3.00 \times 10^8 \text{ m/s}}{\nu_{\text{max}}}$$

Thus, the longest wavelength that will initiate the photoelectric effect in pure sodium is approximately 451.21 nm.

Qn 2.

Calculate the de Broglie wavelength of an electron moving at $\frac{1}{137}$ th the speed of light.

To calculate the de Broglie wavelength (λ) of an electron moving at a certain speed, we can use the de Broglie wavelength formula:

$$\lambda = \frac{h}{p}$$

Where: λ is the de Broglie wavelength. h is the Planck constant, 6.626×10^{-34} J.s. p is the momentum of the electron, which is the product of its mass (m) and velocity (v).

Given that the electron is moving at $\frac{1}{137}$ th the speed of light (c), we have:

$$v = \frac{1}{137}c$$

The mass of an electron (m) is approximately 9.109×10^{-31} kg.

Now, calculate p using m and v :

$$p = m \cdot v = (9.11 \times 10^{-31} \text{ kg}) \cdot \left(\frac{1}{137} \cdot 3.00 \times 10^8 \text{ m/s} \right)$$

Calculate p and then use it to find λ using the de Broglie wavelength formula:

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J.s}}{p}$$

The de Broglie wavelength of the electron moving at $\frac{1}{137}$ th the speed of light is approximately:

$$\lambda = 3.3215 \text{ \AA}$$

Qn 3.

Find the particle's energy for the given system.

A one-particle, one-dimensional system has the potential energy $V = \frac{2c^2 x^2 \hbar^2}{m}$, and its wavefunction is given as $\psi(x) = bxe^{-cx^2}$, where b is a constant, $c = 6.00 \text{ nm}^{-2}$, and $m = 2.00 \times 10^{-27}$ g.

To find the particle's energy, we can use the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

Where: \hbar is the reduced Planck constant, approximately $1.0545718 \times 10^{-34}$ J.s. m is the mass of the particle, which is 2.00×10^{-24} kg. $V(x)$ is the potential

energy given as $\frac{2c^2x^2\hbar^2}{m}$. $\psi(x)$ is the wavefunction given as bxe^{-cx^2} . E is the energy we want to find.

Now, let's calculate the first and second derivatives of the wavefunction $\psi(x)$ with respect to x :

$$\frac{d\psi}{dx} = b(1 - 2cx^2)e^{-cx^2}$$

$$\frac{d^2\psi}{dx^2} = 2bc(cx^2 - 3)xe^{-cx^2}$$

Now, plug these derivatives into the Schrödinger equation:

$$-\frac{\hbar^2}{2m} [2bc(cx^2 - 3)xe^{-cx^2}] + \frac{2c^2x^2\hbar^2}{m} bxe^{-cx^2} = Ebxe^{-cx^2}$$

Now, let's simplify it:

$$-\hbar^2 2bc(cx^2 - 3)xe^{-cx^2} + 2c^2x^3\hbar^2 be^{-cx^2} = Embxe^{-cx^2}$$

Now, let's simplify further:

$$3\hbar^2 c = Em$$

Thus, the particle's energy for the given system is :

$$E = \frac{3\hbar^2 c}{m} = 10^{-25} \text{ J}$$

Qn 4.

Expression for the operator \hat{A} given $\hat{A}f(x) = 3x^2f(x) + 2x\frac{df}{dx}$

If $\hat{A}f(x) = 3x^2f(x) + 2x\frac{df}{dx}$, then the expression for the operator \hat{A} can be obtained by comparing the terms on the left-hand side and the right-hand side of the equation.

We have:

$$\hat{A}f(x) = 3x^2f(x) + 2x\frac{df}{dx}$$

So, the expression for the operator \hat{A} is:

$$\hat{A} = 3x^2 + 2x\frac{d}{dx}$$

5. Give three different operators \hat{A} that satisfy $\hat{A} e^x = e^x$.

Ans. (A) Identity operator (\hat{I}) (B) $\frac{d}{dx}$ (C) Integration Operator $\int dx$

6. Classify each of these operators as linear or nonlinear:

Ans. A linear operator must satisfy the principle of superposition, which means that if you apply the operator to the sum of two functions, it's the same as applying the operator to each function separately and then adding the results.

$$\begin{aligned}
 \text{(a)} \quad & 3x^2 \frac{d^2}{dx^2} \\
 &= 3x^2 \frac{d^2}{dx^2} [f(x) + g(x)] \\
 &= 3x^2 \frac{d^2 [f(x) + g(x)]}{dx^2} \\
 &= 3x^2 f''(x) + 3x^2 g''(x) \\
 &= 3x^2 \frac{d^2 f(x)}{dx^2} + 3x^2 \frac{d^2 g(x)}{dx^2}
 \end{aligned}$$

It is a linear operator.

$$\text{(b)} \quad ()^2(x, y) = (x + y)^2 \neq x^2 + y^2$$

It is a non linear operator.

$$\text{(c)} \quad \int dx$$

$$\int dx [f(x) + g(x)] = \int f(x) dx + \int g(x) dx$$

It is a linear operator.

(d) exp

$$\exp[f(x) + g(x)] \neq \exp f(x) + \exp g(x)$$

It is a non linear operator.

$$(e) \frac{\partial}{\partial x} + \frac{\partial}{\partial y}$$

$$\begin{aligned} \frac{\partial}{\partial x} + \frac{\partial}{\partial y} (f(x,y) + g(x,y)) = \\ \frac{d}{dx} f(x,y) + \frac{d}{dx} g(x,y) + \frac{d}{dy} f(x,y) + \frac{d}{dy} g(x,y) \end{aligned}$$

It is a linear operator.

$$(f) \sum_{x=1}^n$$

$$\sum_{x=1}^n (f(x) + g(x)) = \sum_{x=1}^n f(x) + \sum_{x=1}^n g(x)$$

It is a linear operator

7. Calculate the de Broglie wavelength of an electron and a cricket ball of

mass 500g, both moving at a speed of 500ms^{-1} . What can you infer from the results of this problem?

Ans.
$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Mass of cricket ball (m) = 0.5 kg

Mass of electron (m) = 9.1×10^{-31} kg

Velocity of cricket ball and electron (v) = 500 m/s

h (planck's constant) = $6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$

Electron

$$\lambda = \frac{6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}}{9.11 \times 10^{-31} \text{ kg} \times 500 \text{ m/s}} = 1454.6 \text{ nm}$$

Ball

$$\lambda = \frac{6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}}{0.5 \text{ kg} \times 500 \text{ m/s}} = 2.65 \times 10^{-34} \text{ m}$$

Inference: Ball λ is so high , that we can not observe its quantum nature.

8. Find out whether the following operators are Hermitian operators or not.

(a) potential energy operator , (b) linear momentum operator

Ans.

(a) $\hat{V}(x) = k\hat{x}$

If \hat{x} (position operator) is hermitian then potential energy $\hat{V}(x)$ will be

also hermitian operator

For \hat{x} to be Hermitian we must show that:

$$\langle \phi | \hat{x} \psi \rangle = \langle \psi | \hat{x} \phi \rangle^*$$

LHS:

$$\langle \phi | \hat{x} \psi \rangle = \int \phi^*(x\psi) dx$$

RHS:

$$\langle \psi | \hat{x} \phi \rangle^* = \left(\int \psi^*(x\phi) dx \right)^*$$

Eigenvalues of \hat{x} are real, $x = x^*$:

$$\langle \psi | \hat{x} \phi \rangle^* = \int \psi(x\phi^*) dx$$

$$= \int \phi^*(x\psi) dx$$

$$\therefore \langle \phi | \hat{x} \psi \rangle = \langle \psi | \hat{x} \phi \rangle^*$$

Thus, \hat{x} is Hermitian.

(b)

For \hat{p} to be hermitian we must show the following:

$$\langle \phi | \hat{p} \psi \rangle = \langle \psi | \hat{p} \phi \rangle^*$$

LHS:

$$\langle \phi | \hat{p} \psi \rangle = \int \phi^* (-i\hbar \frac{\partial \psi}{\partial x}) dx$$

RHS:

$$\begin{aligned} \langle \psi | \hat{p} \phi \rangle^* &= \left(\int \psi^* (-i\hbar \frac{\partial \phi}{\partial x}) dx \right)^* \\ &= \int \psi (i\hbar \frac{\partial \phi^*}{\partial x}) dx \\ &= i\hbar \int \psi (\frac{\partial \phi^*}{\partial x}) dx \end{aligned}$$

Using integration by parts gives:

$$\langle \psi | \hat{p} \phi \rangle^* = [\phi^* \psi]_{-\infty}^{\infty} - i\hbar \int \phi^* (\frac{\partial \psi}{\partial x}) dx$$

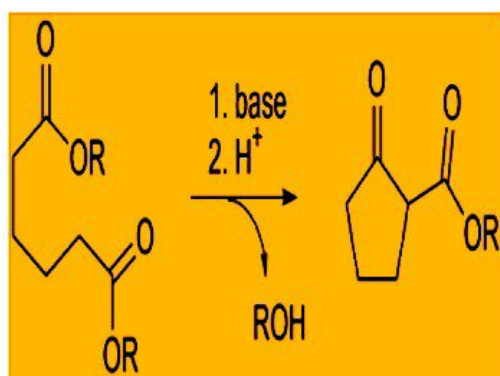
Assume the wavefunctions go to zero at infinity then:

$$\begin{aligned} \langle \psi | \hat{p} \phi \rangle^* &= -i\hbar \int \phi^* (\frac{\partial \psi}{\partial x}) dx \\ &= \int \phi^* (-i\hbar \frac{\partial \psi}{\partial x}) dx \\ \therefore \langle \phi | \hat{p} \psi \rangle &= \langle \psi | \hat{p} \phi \rangle^* \end{aligned}$$

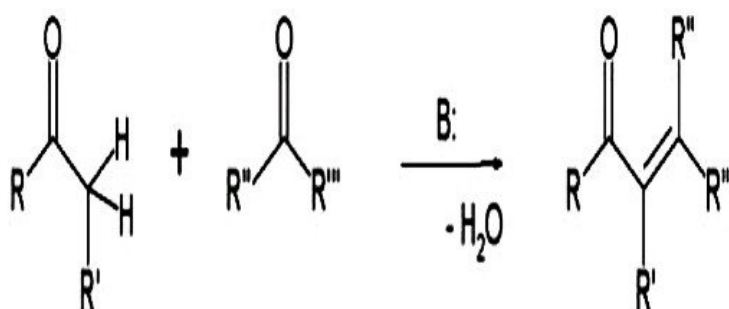
Thus \hat{p} is Hermitian.

Quiz 2 Date: 22/11/2023; 10 Marks

- Q1: How Dieckmann condensation is related to Claisen condensation give examples.
- Ans: A Dieckmann condensation involves two ester groups in the same molecule and yields a cyclic molecule. Its intramolecular Claisen condensation.



- Q2: In which reaction an enolate ion reacts with a carbonyl compound to form a β -hydroxyketone, followed by a dehydration to give a conjugated enone? Write reaction.
- Ans: Aldol condensation.

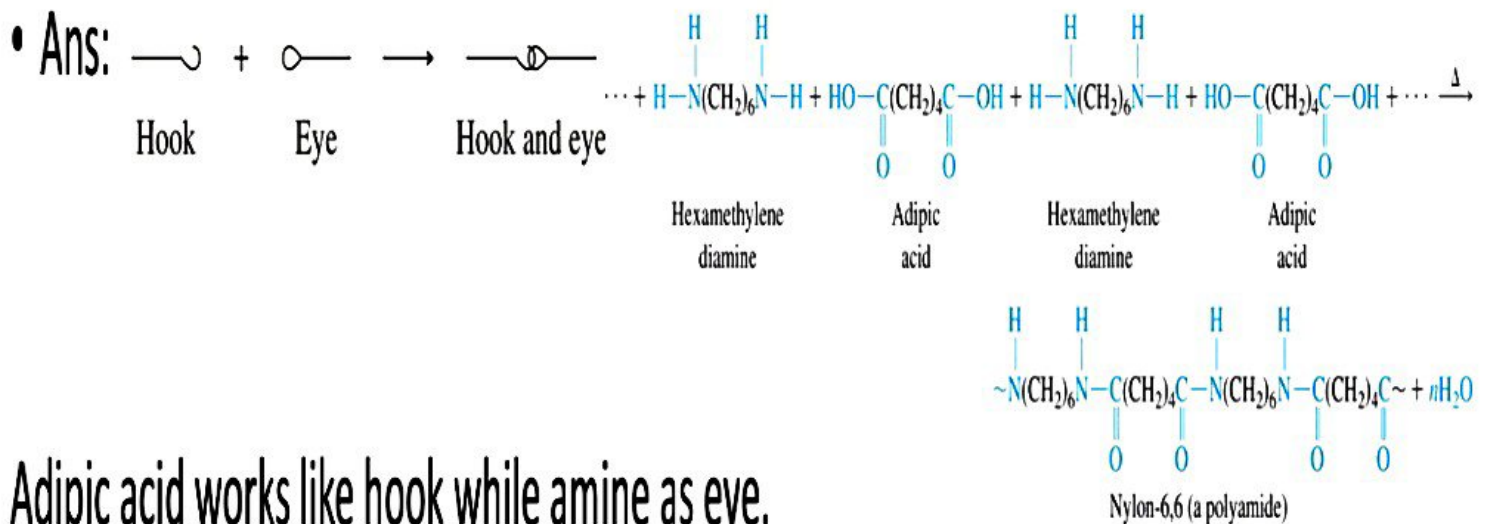


• Q3: What are conducting polymers? Why are they conducting? Write an example.

• Ans: Organic polymers that conduct electricity. Due to conjugation of electron.

polyaniline, polypyrrole..etc

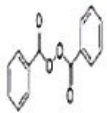





• Q4: What is hook and eye condensation ? How it is related to nylon-6,6? Show pictorially.



Adipic acid works like hook while amine as eye.

• Q5: Why peroxides are used in free radical polymerization? Draw two examples.

• Ans: Peroxides are having weak bonds for easy homolytic cleavage.

Initiator	Radical Generated
Benzoyl peroxide (BPO) 	
Di-tert-butyl peroxide (DTBP) 	
Azobisisobutyronitrile (AIBN) 	

Quiz 1

10 Marks; 07.11.2023; 20 minutes; One line/word answers

Q1 Define spectator ions and its role.

Ans: It directly does not take part in reaction but it affects the activity of nucleophiles.

Q2 Define the term *buffer*.

Ans: A buffer solution consists of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. That is we have a weak acid and its salt or a weak base and its salt

Q3 What are organometallic and metalorganic compounds?

Ans: When Metal connected directly with carbon and when carbon is part of compound but not connected directly with metal.

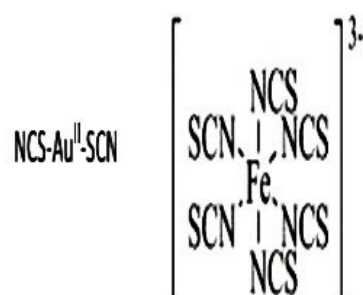
Q4 What is the pH at the equivalence point of the titration?

Ans: The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0

Q5 What is most essential condition for E2 reaction?

Ans: A bimolecular elimination (E2) step takes place when a strong base attacks a substrate in which a leaving group and a hydrogen atom are on adjacent carbon atoms.

Q6 Thiocyanate anion makes two complexes with Au^{+1} and Fe^{+3} write their structures.



Thiocyanate (SCN^-) is a particularly interesting ligand. It is ambidentate, and can bind to metal ions either through the S or the N. Obviously, it prefers to bind to soft metal ions through the S, and to hard metal ions through the N. This can be seen in the structures of $[\text{Au}(\text{SCN})_2]^-$

Q7: Why lanthanides are found in oxides form in nature?

Ans: According to HSAB law, Lanthanides are in +3 oxidation state are hard acids and they make stable complex with O^{2-}

Q8: Why carbon monoxide acts as poison in transition metal catalyzed reactions?

Ans: Most catalytic reactions are governed by low oxidation state transition metals which are soft acids while CO is soft base, that make strong bond and deactivate the catalyst.

Q9 Why 1,2 Shift occurs in carbonations?

Ans: To make higher degree stable carbocation.

Q10 For most Keto-Enol tautomerization equilibria, which form is in greater abundance ?

Ans: Keto