3 (Sem–5) CHM M1

2021

(Held in 2022)

CHEMISTRY

(Major)

Paper : 5·1

(Quantum Chemistry)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

(The symbols used signify their usual meanings)

1. Answer in brief : *(any seven)*   1×7=7

   (a) Write down the term symbol for H_2 in ground state.

   (b) Define eigenvalue and eigenfunction.

   (c) Define complete wave function.

(d) Define the shape of an orbital.

(e) Write the value of the angular function for s-orbital.

(f) Why is Pauli's antisymmetry principle not applicable for bosons ?

(g) Show whether the operator $\hat{o}$ in the equation $\hat{o}\psi = \psi^2$ is linear or not.

(h) The normalization condition is $\int \psi^2 \, d\tau = 1$. State what this condition actually means.

(i) Find the expression for the Hamiltonian operator for a particle of mass m in x-dimension.

2. Answer the following questions : *(any four)*
$$2 \times 4 = 8$$

(a) What do you mean by eigenvalue equation ? Write with example what the constant in the eigenvalue equation indicates.

(b) Show that the wave function for a particle in one-dimensional box of length a, where the potential energy is zero, is not an eigenfunction of the linear momentum operator in one dimension.

(c) Normalise the H-like function $\psi = e^{-n}$.

(d) Taking $2p_z$-orbital as example, write why the p-orbital dumb-bell in shape.

(e) Show that the functions $\sin^{\pi x}/_a$ and $\cos \pi x / a$ are orthogonal within the interval $0 \le x \le a$.

3. What do you mean by complete wave function ? Using Pauli's anti-symmetry principle, prove that no two electrons of an atom can have all the four quantum numbers alike. $1+4=5$

Or

Applying Hückel molecular orbital method, calculate the π-bond energy of ethene. Also find the expressions for the π-molecular orbitals. $3+2=5$

4. (a) Write what you mean by radial distribution function. Find an expression for the radial distribution function. Give the plot of radial distribution function against the radial distance from the nucleus for 1s orbital. State how this plot differs from the plot of square of the radial function against the radial distance.   1+2+1+1=5

   (b) Taking the example of H_2^+, explain how the potential energy diagram can be constructed. What information regarding characterization of a bond can be obtained from this diagram ?

                                                4+1=5

5. Answer either (i) or (ii) and (iii) :

   (i) Calculate the zero-point vibrational energy of Co molecule assuming it to be a harmonic oscillator if the force constant of the bond between the two atoms is 1840 Nm^{-1}. Find the energy difference between two consecutive vibrational levels taking the same assumption.   3

(ii) Find the average value of the distance of the electron from the nucleus of the ground state H-atom.   3

(iii) Write the angular function for s-orbital and hence explain why s-orbital is spherically symmetric.   2

6. (i) A particle of mass m is moving in a one-dimensional box of length a, where potential energy is zero. Calculate the average kinetic energy of the particle.   3

(ii) An electron is confined to a molecule of length $10^{-9} m$. Considering the electron to be a particle in one-dimensional box, where $v = 0$, calculate its minimum energy.   2

7. Answer either (a), (b) and (c) or (d), (e) and (f) :   10

(a) Show graphically how energy is distributed among different wavelengths emitted by a blackbody at a definite temperature. Deduce Planck's radiation law which can explain the above experimental observation.   1+4=5

(b) The work function for *Na* metal is 1.82 *eV*. Calculate. its threshold frequency. 2

(c) Find the lowest kinetic energy of an electron in a three-dimensional box of lengths 1×10^{-13} *cm*, 2×10^{-13} *cm* and 3×10^{-13} *cm* assuming potential energy to be zero. 3

Or

(d) What do you mean by radial function ? Give the plots of radial function against *r* for $n = 2$. State what information you can draw from these plots. 1+1+2=4

(e) State Hund's rule of maximum multiplicity. For the $2P^2$ electrons of the ground state C-atom, the following terms are obtained :

$$^1D_2, \, ^3P_2, \, ^3P_1, \, ^3P_0, \, ^1S_0$$
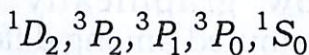
Using Hund's rule, state which of these terms will be the lowest in energy. 2+1=3

(f) Show that the maximum probability of finding the electron of the ground state H-like atom is at $r = a/z$.　　3

8. Answer either (a) and (b) or (c) and (d) : 　10

(a) Show that the total energy of all the radiations emitted by a blackbody is proportional to the 4th power of the absolute temperature of the blackbody. 　4

(b) Show that the Compton shift, observed when a beam of monochromatic X-ray impinges on carbon block and gets scattered, depends on the angle through which scattered radiation is observed, but does not depend on the wavelength of the incident radiation. 　6

Or

(c) Let a cubic box of edge length 1 nm, within which potential energy is zero, contain 10 electrons. Considering ground state, explain with diagram how these electrons occupy different states. 　3

(d) Write the approximations of the Hückel molecular orbital theory. Explain, what you mean by space quantization ?

4+3=7

Total number of printed pages–7

2021

(Held in 2022)

CHEMISTRY

(Major)

Paper : 5·2

(Physical Chemistry)

Full Marks : 60

Time : Three hours

*The figures in the margin indicate
full marks for the questions.*

1. Answer in brief :   1×7=7

   (a) State why a heterogeneous catalyst is
   often taken in the form of finely divided
   powder rather than as smooth surface.

   (b) State what is meant by quantum yield
   for photochemical reactions.

(c) Under what condition would the Lindemann theory of unimolecular gaseous reactions show second-order kinetics ?

(d) An iceberg is floating in the lake. If one considers the lake, iceberg and atmosphere as a one system, what are the number of phrases ?

(e) State how the rate constant of a reaction between ions varies with ionic strength of the solution.

(f) How many components are present in the following equilibria ?

$$CaCO_3 \ (s) \rightleftharpoons CaO \ (s) + CO_2 \ (g)$$

(g) Why does physisorption decrease with increase of temperature ?

2. Answer the following questions : 2×4=8

(a) Express Eyring equation regarding activated complex theory in terms of entropy and enthalpy of activation.

(b) Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. Explain.

(c) Using Clausius-Clapeyron equation, explain the nature of variation of vapour pressure with temperature.

(d) For a first-order reaction, the activation energy is $108.4 \, kJ \, mol^{-1}$. What is the enthalpy of activation of the reaction at $130°C$?

3. Answer *any three* of the following questions : $\qquad$ 5×3=15

(a) Write the postulates of hard-sphere collision theory. On the basis of collision theory, find an expression for the rate constant of the elementary biomolecular gaseous reaction $A + B \rightarrow$ products.
$\qquad$ 2+3=5

(b) On the basis of the postulates of Langmuir's adsorption theory, deduce the Langmuir adsorption isotherm. How can the monolayer volume Vm be obtained from this isotherm ?

(c) The decomposition of HI takes place by the following mechanism :

$$HI + hv \rightarrow \dot{H} + \dot{I}$$
$$\dot{H} + HI \rightarrow H_2 + \dot{I}$$
$$\dot{I} + \dot{I} \rightarrow I_2$$
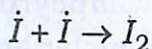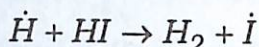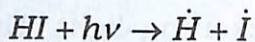
Find an expression for the rate of the reaction. Also find the quantum efficiency of the reaction.

(d) Derive Gibbs adsorption isotherm thermodynamically for the adsorption of a solute on the surface of a liquid.

(e) Draw energy profile diagrams for exothermic and endothermic reactions. Show that for a gaseous bimolecular reaction

$$A(g) + B(g) \rightarrow (AB)^{++} \rightarrow \text{Product}$$
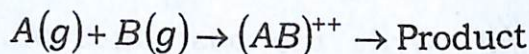
$Ea = \Delta H_{m^{++}} + 2RT$, where the subscript m stands for molar.   1+1+3=5

4. Answer **either** (a) and (b) **or** (c) and (d) :
                                        5+5=10

(a) State the reason why light emission during phosphorescence is slow.

State Stark-Einstein law of photochemical equivalence. Under what condition of radiation, this law is applicable ?   1+4=5

(b) Discuss, how ionic strength influences the rate of a chemical reaction between ions. 5

(c) The following mechanism has been proposed for enzyme catalysis :

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} P + E$$
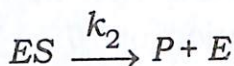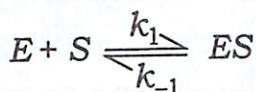
Using steady state approximation for $[ES]$, show that the reaction rate is given by

$$r = \frac{k_2 [E]_0 [S]}{k_m + [S]}$$

where the symbols have their usual meanings. Discuss the rate when $k_m \gg [S]$. 5

(d) Derive Gibbs phase rule. How is the number of component C calculated for systems involving ions and having some chemical reactions equilibrium among the constituents ? Hence explain why $KCl - NaCl - H_2O$ is a 4-component system whereas $KCl - NaBr - H_2O$ is a 3-component system. 2+1½+1½=5

Contd.

5. Answer *either* (a) and (b) *or* (c) and (d) :
5+5=10

(a) The photochemical dissociation of gaseous *HI* to form hydrogen and iodine atoms, requires radiation of 404nm or less.

(i) Determine the molar heat of dissociation of *HI*.

(ii) If radiation of 253·7nm is used, how much energy will appear as kinetic energy of atoms ?
2+3=5

(b) Derive BET equation for multilayer adsorption of an adsorbate on a. adsorbent.
5

(c) Explain how one can calculate the surface area of an adsorbent, provided the monolayer volume *Vm* of the adsorbate gas was determined using either BET or Langmuir isotherm.

Discuss different steps of the Langmuir-Hinshelwood mechanism of gaseous reactions taking place on solid surface.
2+3=5

(d) What do you mean by solid compound with congruent melting point? Draw the phase diagram of such a system forming two such compounds. Explain the diagram.   2+3=5

6.   What is the role of photosensitizer in the photochemical reaction? What is quenching? Discuss the role of nitrogen oxides and chlorofluorocarbons in ozone layer depletion. Explain the phenomenon of fluorescence with the help of Jablonski diagram.   2+2+3+3=10

3 (Sem–5) CHM M3

2021

(Held in 2022)

CHEMISTRY

(Major)

Paper : 5·3

(Organic)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : *(any seven)*
   $1 \times 7 = 7$

   (a) Give the product of the following reaction :

   $$CH_3 - CH = CH - COOH \xrightarrow[\text{2) } H_3O^+]{\text{1) } LiAlH_4, \text{ Ether}}$$
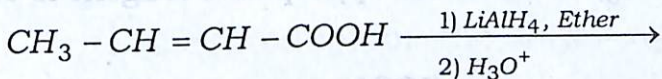
   (b) What happens when acetylene and H_2S are passed over alumina at $400°C$?

(c)   Why is naphthalene less aromatic than benzene?

(d)   Write the IUPAC name of

(e)   How is Lindlar's catalyst prepared?

(f)   What is Schiff's base?

(g)   Define 'frontier orbital' with appropriate example.

(h)   Write 'aciform' structure of nitromethane.

(i)   Why does diethyl malonate undergo alkylation?

(j)   Write the appropriate reagent to convert
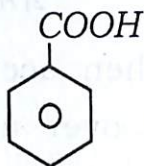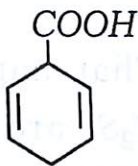
(k) Why does electrophilic aromatic substitution of indole occur preferably at the 3-position ?

2. Answer the following questions : *(any four)*
$2 \times 4 = 8$

(a) What happens when secondary amines react with HNO_2 ? Write the equation.

(b) How will you synthesise CH_3CH_2SH from $H_2N - \underset{\underset{S}{||}}{C} - NH_2$? Write the reaction.

(c) Which position(s) of quinoline undergo(es) nucleophilic aromatic substitution easily ? Give reason.
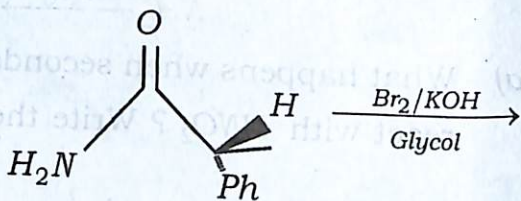
(d) Explain the basic character of pyridine.

(e) Write the product of the following reaction :

$$CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow[Liq\ NH_3]{Na}$$

3. Answer the following questions [*any* *one* from (a) and (b) and *two* from (c), (d) and (e)] : 5+(5×2)=15

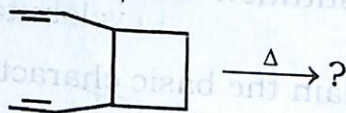(a) Write the product of the following reaction along with mechanism :

Also justify the configuration of the product. 1+2+2=5

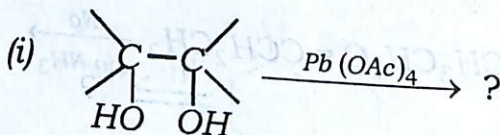(b) What will happen if 3-hydroxy-1,5-diene is heated ? Propose a mechanism. Write the product (s) expected to be formed in the following reaction : 2+2+1=5
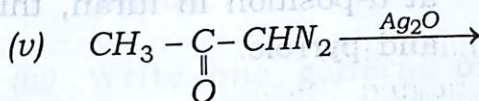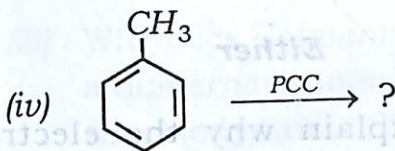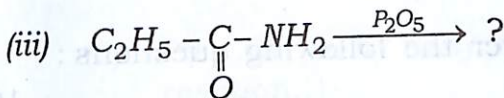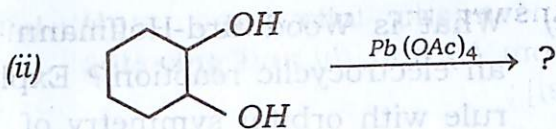

(c) Complete the following reactions : 1×5=5

(i)

(ii)

$$\xrightarrow{Pb\,(OAc)_4} ?$$

(iii) $C_2H_5 - \underset{\underset{O}{\|}}{C} - NH_2 \xrightarrow{P_2O_5} ?$

(iv)

$$\xrightarrow{PCC} ?$$

(v) $CH_3 - \underset{\underset{O}{\|}}{C} - CHN_2 \xrightarrow{Ag_2O}$
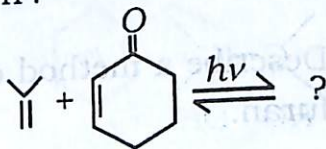
(d) Explain why (2E,4Z) hexadiene thermally cyclizes to give cis-3,4-dimethyl-cyclobutane.
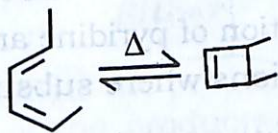
Write the product of the following reaction :   4+1=5

$$\xrightleftharpoons{h\nu} ?$$

(e) What is Woodward-Hoffmann rule of an electrocyclic reaction ? Explain the rule with orbital symmetry of 1,3-butadiene. 5

4. Answer the following questions :

10×3=30

Either

(a) *(i)* Explain why the electrophilic substitution takes place preferably at α-position in furan, thiophene and pyrrole. 3
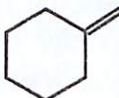
(ii) Pyrrole is acidic in character like phenol. Explain. 2

(iii) Describe the mechanism of nitration of pyridine and justify the positions where substitution takes place. 5

Or

(b) *(i)* Describe a method of synthesis of furan. 3

(ii) How can you prepare the following ? 2

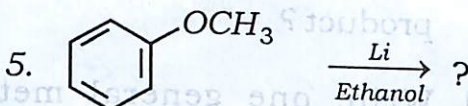(1) by Wittig reaction

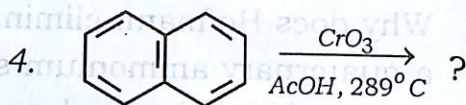(2) Ph–COOMe by Baeyer-Villiger reaction.
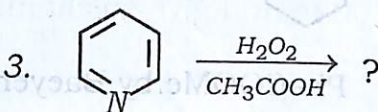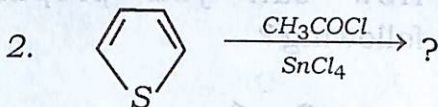
(iii) Why does Hofmann elimination of a quaternary ammonium salt give thermodynamically less stable alkene as the predominant product ? 2

(iv) Write one general method of synthesis of thiols, RSH. How can RSH be converted to (1) RSSR, and (2) RSR ? 1+1+1=3

Either

(c) (i) Write the products and the names of the products for the reactions given below : 1×5=5

1. $\xrightarrow{SeO_2}$?

2. $\xrightarrow[\text{SnCl}_4]{\text{CH}_3\text{COCl}}$?

3. $\xrightarrow[\text{CH}_3\text{COOH}]{\text{H}_2\text{O}_2}$?

4. $\xrightarrow[\text{AcOH, 289}^\circ C]{\text{CrO}_3}$?

5. $\xrightarrow[\text{Ethanol}]{\text{Li}}$?

(ii) Why cannot $LiAlH_4$ be used in protic solvent ?   1

(iii) Identify A and B in the following reactions (Give the structure and name) :   2

$A \xleftarrow[\text{Pt}]{\text{H}_2}$ $\xrightarrow[\text{CH}_3\text{OH}]{\text{H}_2-\text{Pd}} B$
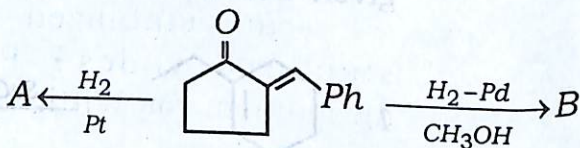
(iv) Explain why furan is less reactive than pyrrole. 2

Or

(d) *(i)* Predict the product of the following reaction and give mechanism of it : 3
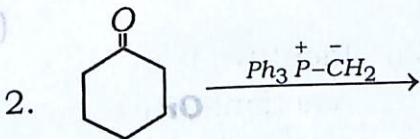

$$\overset{\oplus}{N_2} \overset{\ominus}{Cl}$$

benzene ring with $N_2^{\oplus} Cl^{\ominus}$ at top and CH_3 at bottom, $\xrightarrow{CuCl}$?
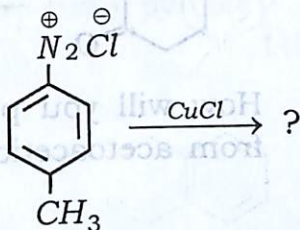
(ii) Give the products in each of the following reactions : 2

1. cyclohexanone $\xrightarrow{\quad Me_2 \overset{\oplus}{S} - \overset{\ominus}{CH_2} \quad}$

2. cyclohexanone $\xrightarrow{\quad Ph_3 \overset{+}{P} - \overset{-}{CH_2} \quad}$
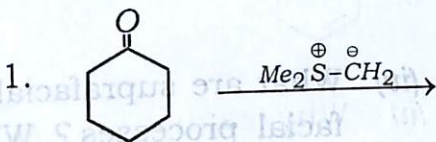
(iii) What are stabilized and non-stabilized ylides ? Propose a mechanism for Wittig reaction. 2+3=5

Either

(e) (i) Write the product and name the rearrangement involved : 2

$$\xrightarrow[H^+]{NaOH}$$
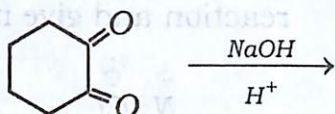
(ii) How will you prepare pentanone from acetoacetic ester ? 2

(iii) Why is K_b of pyridine 2.3×10^{-9} and that of pyrrole 2.5×10^{-4} ?

1

(iv) What are suprafacial and antarafacial processes ? Which is more common and why ?

$$(1+1)+(1+2)=5$$

Or

(f) (i) How is Jones reagent different from Collins reagent ? Propose a mechanism for the conversion of a primary alcohol to aldehyde with a Cr(VI) reagent. 2+3=5

3 (Sem–5) CHM M3 /G   10

(ii) Write the IUPAC names of pyrrole, thiophene and pyridine. Write down the steps involved in the Bischler-Napieralski reaction leading to synthesis of isoquinoline. Why is indole less reactive than pyrrole ?

$$1\frac{1}{2}+2+1\frac{1}{2}=5$$

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3 (Sem–5) CHM M 4

2021

(Held in 2022)

CHEMISTRY

(Major)

Paper : 5·4

(Inorganic Chemistry)

Full Marks : 60

Time : Three hours

**The figures in the margin indicate
full marks for the questions.**

Objective-type questions : *(Choose the correct
answers)* $1 \times 7 = 7$

1. Three-fold axes of symmetry are present in

    (a) octahedron

    (b) tetrahedron

    (c) trigonal bipyramid

    (d) All of the above

2. The point group symmetry of the complex

$$H_3N \diagdown \underset{Pl}{\diagup} \diagup Cl$$
$$H_3N \diagup \overset{Pl}{\diagdown} Cl$$

is

(a) T_d

(b) D_{4h}

(c) C_{2v}

(d) D_{2h}

3. TEL is an/a

(a) ionic organometallic compound

(b) sigma-bonded organometallic compound

(c) electron-deficient organometallic compound

4. Vitamin B12 contains

(a) Zn

(b) Fe

(c) Co

(d) Mo

5. The metalloprotein which is involved in the storage of iron in living systems is

   (a) ferredoxin

   (b) haemoglobin

   (c) myoglobin

   (d) ferritin

6. The catalytically important metal in Ziegler-Natta polymerization is

   (a) Rh

   (b) Al

   (c) Ti

   (d) Pd

7. Each of the following contains a six-membered ring. Which molecule will have a six-fold (C_6) principal notation axis ?

   (a) Borazine

   (b) Pyridine

   (c) Benzene

   (d) S_6-molecule

Very short answer-type questions : $2\times4=8$

8. Draw the structure of $Fe_2(CO)_9$ and verify the EAN rule for this complex.

9. Show all the symmetry elements present and assign the point-group symmetry of boric acid, $B(OH)_3$.

10. What is the $Cr-Cr$ bond order in the compound $Cr_2(N-O_2(CH_3)_4(H_2O)_2$?

11. Predict the magnetic properties of the species $[COF_6]^{-3}$ and $[CO(NH_3)_6]^{+3}$.
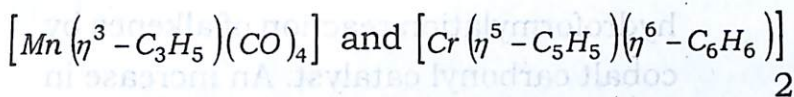
Short answer-type questions : *(any three)*

$5\times3=15$

12. *(a)* Explain why CO is a strong field ligand while I^- is a weak field ligand.

   (b) Write a short note on dioxygen toxicity.

   (c) Discuss the applications of organometallic compounds of zinc.

(d) Discuss the Dewar-Chatt-Duncanson theory of bonding in metal olefin complexes.

(e) (i) Explain the basis of 18-electron rule for octahedral organic complexes. 3

(ii) Verify the EAN rule for the organometallic compounds

$$\left[Mn\left(\eta^3 - C_3H_5\right)(CO)_4\right] \text{ and } \left[Cr\left(\eta^5 - C_5H_5\right)\left(\eta^6 - C_6H_6\right)\right]$$

2

13. Answer the following essay-type questions : *(any three)* 10×3=30

(a) (i) Discuss the conditions under which a group of symmetry elements forms a group.

(ii) Find the symmetry elements and respective point groups for the following molecules :

(1) CO_2

(2) $\left[PtCl_4\right]^{-2}$

(3) NH_3
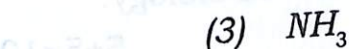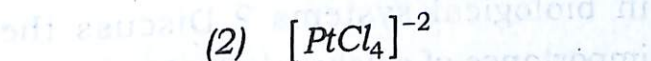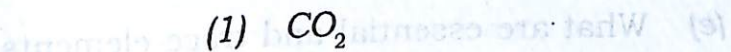
(b) (i) Discuss the functions of haemoglobin and myoglobin. Explain the terms 'cooperative effect' and 'Bohr effect'. 6

(ii) Give an account of toxicity arising from dioxygen in the living system. 4

(c) Discuss the catalytic cycle of hydroformylation reaction of alkenes by cobalt carbonyl catalyst. An increase in carbon monoxide (CO) partial pressure decreases the rate of cobalt catalyzed hydroformylation of 1-pntene suggest an interpretation of this observation. 6+4=10

(d) What are symmetry elements and symmetry operations ? Illustrate all possible symmetry elements of an octahedral complex (ML_6) with the help of a diagram. 10

(e) What are essential and trace elements in biological systems ? Discuss the importance of calcium in biology. 5+5=10

(f) Compare and contrast homogeneous and heterogeneous catalysis. Discuss the role of transition metal complexes as homogeneous catalysts for hydrogenation of alkenes by taking suitable examples. 3+7=10

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