PREFACE

The principal purpose of writing this book **"TIFR"** is to cater to the needs of the candidates aspiring for **"TIFR GS -CHEMISTRY"** exam. It provides explanations of the previous year questions from the year 2010 to 2026. To help students, we have compiled this book in a user-friendly and well-structured manner. Book includes chapters according to the main topics and each chapter is further subdivided into units. This fine sorting of questions will help the students to prepare for each subtopic effectively.

The book will help the reader to understand and solve all the previous year questions. Regular practice is the key to success in any competitive exam, and this book allows you to hone your problem-solving skills.

We have tried to keep the material as simple as possible with easy explanations. The practice of these questions will help the students not only for TIFR exam but also for other competitive exams like CSIR NET, GATE, PhD entrances, etc.

A word or suggestion from your side may add another feather to the cap in the compilation of questions in this book. The author looks forward to the comments, suggestions, and criticism from the students.

Constructive suggestions and user feedback would be highly appreciated, gratefully acknowledged, and suitably incorporated. We wish all the best to all aspirants who are preparing for these exams.

SYLLABUS

The syllabus for the written test in Chemistry is similar to the typical standard syllabus followed in any Indian university for the B.Sc. and M.Sc. degree course. The questions are aimed at testing the basic understanding and knowledge in the areas of physical, organic, inorganic, analytical, electro and quantum chemistry, biophysics, thermodynamics, spectroscopy (NMR, fluorescence, IR, UV and X-ray), logic and statistics and mathematical methods.

EXAM PATTERN

This is a multiple-choice question paper with only ONE section having a total of 40 questions. Each correct answer will get 3 marks. Every wrong answer will get a -1 mark. Marks are not awarded or deducted when a question is not attempted. It is better not to answer a question if you are not sure.

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SECTION-I

PHYSICAL CHEMISTRY

TIFR CHEMISTRY: NUMBER OF QUESTIONS ASKED IN TIFR EXAM (2010 to 2026)

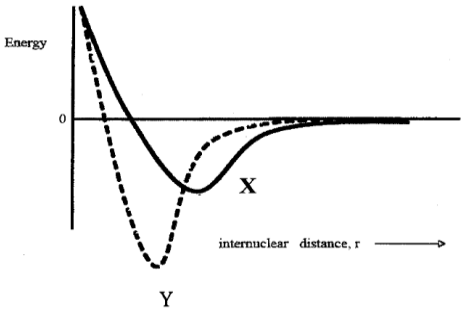
	TOPIC	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
1	STRUCTURE & QUANTUM CHEMISTRY	2	1	5	5	3	5	3	5	5	4	3	4	3	10	5	6	5
2	GROUP THEORY	-	1	-	2	-	2	1	-	1	1	1	-	-	-	1	1	1
3	MOLECULAR SPECTROSCOPY	3	-	2	-	4	1	1	-	3	3	1	-	2	-	-	2	3
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	UNIT 4.1: CHEMICAL THERMODYNAMICS	1	2	3	4	3	2	5	4	2	5	3	3	3	2	3	2	3
	UNIT 4.2: CHEMICAL EQUILIBRIUM	1	-	-	2	-	-	-	1	-	-	-	1	3	-	-	-	1
	UNIT 4.3: ELECTROCHEMISTRY	3	3	3	-	4	2	1	2	2	1	-	1	1	2	3	1	-
	UNIT 4.4: PHASE EQUILIBRIUM	-	1	1	-	-	1	2	-	1	1	-	-	2	-	1	1	-
	UNIT 4.5: STASTICAL THERMODYNAMICS	-	-	-	-	1	1	-	-	-	-	-	1	-	2	1	2	4
5	KINETICS	3	4	3	2	2	5	2	1	3	3	3	3	1	1	2	3	3
6	SURFACE & INTERFACES	2	3	1	3	3	2	2	1	1	1	-	-	-	1	2	2	2
7	MATHEMATICS	3	6	3	1	3	2	3	3	3	1	1	2	2	6	3	4	3

CHAPTER-1 STRUCTURE AND QUANTUM CHEMISTRY

PREVIOUS YEAR EXAM QUESTIONS

(TIFR 2010)

1. Consider the two diatomic molecules CN and CN^-, and the potential energy diagram shown below.



Y

Which of the following is the correct statement?

(a) Bond order of CN is 2.5 and the curve Y corresponds to CN.

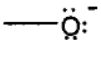
(b) Bond order of CN is 3 and the curve X corresponds to CN.

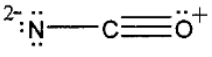
(c) Bond order of CN^- is 3 and the curve Y corresponds to CN^-.

(d) Bond order of CN^- is 2.5 and the curve X corresponds to CN^-.

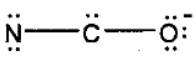
(TIFR 2010)

2. In valence-bond calculations, contributions of various resonance structures are used to calculate the total energy of a molecule. Given below are four resonance structures of the cyanate ion. Which one contributes least to the total energy?

(a) 

(b) 

(c) 

(d) 

(TIFR 2011)

3. An electronic state of a hydrogen atom is prepared to be a superposition energy of the eigenstates of the hydrogen atom, and for which the normalized wave function is written as:

$\phi = \frac{1}{\sqrt{2}}|1s\rangle + \frac{1}{\sqrt{4}}|2s\rangle + C_{3s}|3s\rangle$

Here $|1s\rangle, |2s\rangle$ and $|3s\rangle$ are the exact energy eigenstates of the hydrogen atom, and C_{3s}, is a constant. What would be the average value of energy, associated with this wavefunction ϕ, in a.u.?

(a) $-0.2951\ a.u.$ (b) $-0.4161\ a.u.$

(c) $-0.2269\ a.u.$ (d) $-0.3929\ a.u.$

(TIFR 2012)

4. The transition probability for spontaneous emission from state m to state n is given by an expression

$A_{m\to n} = \left(\frac{64\pi^4 v_{mn}^3}{3hc^3}\right) \cdot \left(\left|\langle m|\hat{d}|n\rangle\right|^2\right)$

Where, V_{mn} is the frequency of transition, and the term in the parenthesis is the transition dipole. Assuming that the magnitude of the transition dipole is same for all types of transitions, arrange the average lifetimes for the electronic, vibrational, and rotational transitions in the proper order.

(a) vibrational < rotational < electronic

(b) electronic < vibrational < rotational

(c) rotational < vibrational < electronic

(d) electronic < rotational = vibrational

(TIFR 2012)

5. In a spherical polar coordinate system, a point A at (x, y, z) in the Cartesian coordinate system can be described by (r, θ, ϕ) where r, θ, and ϕ have their usual meaning. Expression for the volume of an infinitesimally small cube confined by dx, dy, and dz in terms of the spherical coordinate system is given by

(a) $drd\theta d\phi$ (b) $rsin\theta drd\theta d\phi$

(c) $r^2 \sin^2\theta\, drd\theta d\phi$ (d) $r^2 \sin\theta\, drd\theta d\phi$

(TIFR 2012)

6. The degeneracy of the energy level $12h^2/8ma^2$ of a particle in a three dimensional cube of length "a" is

(a) 1 (b) 3

(c) 6 (d) 12

(TIFR 2012)

7. For the above, if the states were non-degenerate and with energy eigenvalues E and -E respectively, then what would be the expectation value of the energy?

(a) 3E (b) 5E

(c) E (d) None of the above

(TIFR 2012)

8. A quantum mechanical state Q is a superposition of two normalized energy eigenstates A and B in an amplitude ratio 2:1. If the two states are degenerate with a common eigenvalue E, what is the energy of the state Q?

(a) 0 (b) E

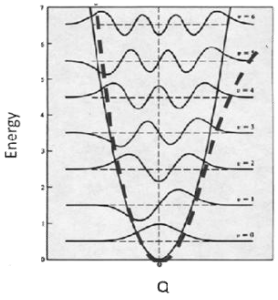
(c) 5E (d) 3E

(TIFR 2013)

9. Given three systems, A, B, and C, what could be they if the spacing between the neighbouring energy levels in A decreases with increasing energy, while that for B is constant, and that for C increases with increasing energy?
   (a) A = particle in a one-dimensional box, B = harmonic oscillator, C = electron in hydrogen atom
   (b) A = electron in hydrogen atom, B = harmonic oscillator, C = particle in a one-dimensional box
   (c) A = particle in a one-dimensional box, B = electron in hydrogen atom, C = harmonic oscillator
   (d) A = electron in hydrogen atom, B = particle in a one-dimensional box, C = harmonic oscillator

(TIFR 2013)

10. Shown below in solid-line is the harmonic potential of a quantum oscillator for a diatomic molecule. If the harmonic potential is suddenly transformed into Morse potential shown in dashed-line how would the zero point energy and shape of wave functions change?



   (a) Zero-point energy remains the same and wave functions do not change.
   (b) Zero-point energy remains the same but wave function reflects a change on the high Q side.
   (c) Zero-point energy changes and wave function reflects a change on the high Q side.
   (d) Potentials never reflect any change in the shape of the wave function

(TIFR 2013)

11. Consider a classical harmonic oscillator with a mass m and a force constant k oscillating with a frequency v. Which of the following statements is NOT true for this system?
   (a) v increases ifm decreases.
   (b) The oscillator is most likely to be found at its equilibrium position.
   (c) The acceleration is maximum at its turning points.
   (d) v does not depend on how large the amplitude of the oscillation is.

(TIFR 2013)

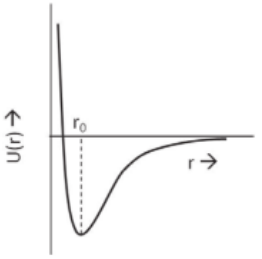
12. What is the degeneracy of the energy level with n-6 (n being the principal quantum number) in a hydro genic atom or ion?
   (a) 16 (b) 9
   (c) 36 (d) 25

(TIFR 2013)

13. Which of the following experimental observations best demonstrates the wavelike character of electrons?
   (a) The photoelectric effect
   (b) The flow of electrons in a metal wire
   (c) The diffraction pattern of electrons scattered from a crystalline solid
   (d) The deflection of an electron beam by electrical plates

(TIFR 2014)

14. The potential energy of a diatomic molecule, as a function of the inter nuclear separation r, is approximated as
   $U(r) = \frac{A}{r^a} - \frac{B}{r^b}$
   Where A and B are positive constants and $a > b$



   As shown in the above figure, r_0 is the equilibrium bond length. What is the energy necessary to break the bond from its equilibrium position?
   (a) $\frac{A}{r_0^a} - \frac{B}{r_0^b}$
   (b) $\frac{B}{r_0^b} - \frac{A}{r_0^a}$
   (c) $\frac{A}{r_0^a}\left(\frac{a}{b} - 1\right)$
   (d) both B and C

(TIFR 2014)

15. Transition states in chemical reactions are generally not directly observed in experiments because
   (a) their structures are different from reactants and products
   (b) they have the highest kinetic energy and hence difficult to capture
   (c) they have the highest potential energy and their lifetimes are short
   (d) all of the above

(c) $\frac{3}{2\beta}, \frac{1}{2\beta}$ (d) $\frac{3}{2\beta}, \frac{3}{2\beta}$

(TIFR 2026)

75. Consider two electrons in two different spatial orbitals whose spins are given as follows:

$$\psi_1 = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}; \psi_2 = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}$$

where ↑ represents the up spin and ↓ represents the down spin. What can we say about the spin multiplicities of the two states?

(a) Singlet; Triplet (b) Triplet; Singlet
(c) Triplet; Triplet (d) Singlet; Singlet

Answer Key									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(c)	(b)	(a)	(b)	(d)	(a)	(d)	(b)	(b)	(d)
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(b)	(c)	(c)	(d)	(c)	(a)	(b)	(b)	(d)	(c)
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
(a)	(c)	(c)	(a)	(d)	(b)	(c)	(b)	(d)	(b)
31	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
(d)	(c)	(b)	(b)	(c)	(d)	(d)	(d)	(d)	(c)
41	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
(a)	(d)	(c)	(d)	(a)	(b)	(c)	(b)	(d)	(b)
51	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**
(c)	(c)	(a)	(b)	(b)	(c)	(c)	(b)	(c)	(a)
61	**62**	**63**	**64**	**65**	**66**	**67**	**68**	**69**	**70**
(d)	(c)	(c)	(a)	(c)	(a)	(b)	(d)	(b)	(c)
71	**72**	**73**	**74**	**75**					
(c)	(c)	(a)	(d)	(a)					

SOLUTIONS

1. Correct Answer is (c)

Bond orders

- CN (9 valence electrons): $\sigma 2s^2\ \sigma^*2s^2\ \pi 2p^4\ \sigma 2p^1$, so bond order = (7 − 2)/2 = 2.5
- CN^- (10 valence electrons, like N_2): $\sigma 2s^2\ \sigma^*2s^2\ \pi 2p^4\ \sigma 2p^2$, so bond order = (8 − 2)/2 = 3

Curves

Curve Y has the deeper well with its minimum at the shorter internuclear distance. That means the stronger, shorter bond, so Y is CN^- (bond order 3) and X is CN (bond order 2.5).

2. Correct Answer is (b)

More electronegative element has negative charge. More stable compound has less energy and unstable compound has more energy.

3. Correct Answer is (a)

normalized wavefunction; $C_1^2 + C_2^2 + C_3^2 = 1$

$\left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{4}}\right)^2 + C_3^2 = 1$

$C_3^2 = \frac{1}{4}$

Energy of hydrogen atom in a.u is

$E = -0.5\left(\frac{z^2}{n^2}\right)$

Average energy;

$< E > = C_1^2 E_1 + C_2^2 E_2 + C_3^2 E_3$

$= \left(\frac{1}{\sqrt{2}}\right)^2 \left(-\frac{0.5}{1^2}\right) + \left(\frac{1}{\sqrt{4}}\right)^2 \left(-\frac{0.5}{2^2}\right) + \left(\frac{1}{4}\right)\left(-\frac{0.5}{3^2}\right)$

$= -0.2951 a.u$

4. Correct Answer is (b)

Assuming the magnitude of the transition dipole moment (|*dmn*|) is the same for all transitions, the transition probability is directly proportional to the cube of the transition frequency (*vmn*3).

- Electronic transitions: ~$10^{15} Hz$
- Vibrational transitions: ~$10^{13} Hz$
- Rotational transitions: ~$10^{11} Hz$

Since the transition probability is proportional to the cube of the frequency, the order of the average lifetimes (which are inversely proportional to the transition probability) is:

electronic < vibrational < rotational

5. Correct Answer is (d)

The Jacobian of the transformation x = r sinθ cosϕ, y = r sinθ sinϕ, z = r cosθ is

$$\left|\frac{\partial(x,y,z)}{\partial(r,\theta,\varphi)}\right| = r^2 sin\theta$$

Geometrically, a small box at (r, θ, ϕ) has three edge lengths:

- Radial: dr
- Polar direction: r dθ
- Azimuthal direction: r sinθ dϕ (the circle at that latitude has radius r sinθ)

Multiplying them gives dV = (dr)(r dθ)(r sinθ dϕ) = r^2 sinθ dr dθ dϕ.

6. Correct Answer is (a)

Energy of a particle in 3 dimensional is ;

$E = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8ma^2}$

$= \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8ma^2} = \frac{12h^2}{8ma^2}$

$n_x^2 + n_y^2 + n_z^2 = 12$

$2^2 + 2^2 + 2^2 = 12$

If $n_x = n_y = n_z$ then degeneracy is 1

7. Correct Answer is (d)

If the two non-degenerate energy eigenstates have eigenvalues:

$$\boldsymbol{E_1 = E}, \quad \boldsymbol{E_2 = -E}$$

and the system is in a general state

$$|\boldsymbol{\psi} > = \boldsymbol{c_1}|\boldsymbol{E} > + \boldsymbol{c_2}| - \boldsymbol{E} >,$$

then the expectation value of energy is

$$\langle \boldsymbol{H} \rangle = |\boldsymbol{c_1}|^2 \boldsymbol{E} + |\boldsymbol{c_2}|^2(-\boldsymbol{E})$$

$$\langle \boldsymbol{H} \rangle = \boldsymbol{E}(|\boldsymbol{c_1}|^2 - |\boldsymbol{c_2}|^2)$$

Since the probabilities depend on the given state, the expectation value is **not necessarily 3E, 5E, or E**. For an equal superposition, it would be 0, but that is also not among the options.

8. Correct Answer is (b)

$Q = \frac{2}{\sqrt{5}} \left| A > + \frac{1}{\sqrt{5}} \right| B >$

The energy operator H^ acting on a state $|A\rangle$ gives the energy eigenvalue E, and similarly, acting on state $|B\rangle$ also gives E. Therefore, the expectation value of the energy operator H^ for the state $|Q\rangle$ is:

$< Q|H|Q > = \left(\frac{2}{\sqrt{5}}\right)^2 E + \left(\frac{1}{\sqrt{5}}\right)^2 E$

$= \frac{4}{5}E + \frac{1}{5}E = E$

9. Correct Answer is (b)

The energy of a hydrogen atom and its neighbouring distance have an inverse relationship. This means:

Lower energy: Corresponds to a larger neighbouring distance between the electron and the nucleus.

Higher energy: Corresponds to a smaller neighbouring distance between the electron and the nucleus.

In harmonic oscillator neighbouring distance constant. In one dimension with increasing energy neighbouring distance increases.

10. Correct Answer is (d)

The **potential-energy curve itself does not directly determine or "reflect" the wavefunction shape** in the sense stated by the options. The wavefunction is obtained by solving the **Schrödinger equation** for the complete potential.

11. Correct Answer is (b)

The probability of finding the oscillator at different positions depends on its energy state. At higher energy states, the oscillator is equally likely to be found anywhere within its range of motion.

12. Correct Answer is (c)

In a hydrogenic atom degeneracy $= n^2$

$= 6^2 = 36$

13. Correct Answer is (c)

Electrons exhibit wave-particle duality. Their wavelike nature is demonstrated by diffraction and interference, just like light waves.

(A) Photoelectric effect → demonstrates the particle nature of light, not the wave nature of electrons.

(B) Flow of electrons in a metal wire → shows electron transport, not specifically wave behavior.

(C) Electron diffraction by a crystal → electrons produce a diffraction pattern, directly demonstrating their de Broglie wave nature.

(D) Deflection by electric plates → demonstrates the charged-particle nature of electrons.

14. Correct Answer is (d)

At equilibrium bond length r_0 the potential energy is minimum, meaning the molecule is stable. Therefore, the potential energy at r_0 is;

$U(r_0) = \frac{A}{r_0^a} - \frac{B}{r_0^b}$

To break the bond, we need to consider the dissociation limit where the molecule completely dissociates into two separated atoms. In this case, the potential energy approaches zero, as the atoms are infinitely far apart. So, at the dissociation limit, the potential energy is;

$U(\infty) = 0$

Energy to break the bond $U(\infty) - U(r_0) = 0 - \left(\frac{A}{r_0^a} - \frac{B}{r_0^b}\right)$

$= \frac{B}{r_0^b} - \frac{A}{r_0^a}$

15. Correct Answer is (c)

A transition state sits at the top of the potential energy barrier along the reaction coordinate. Two facts about it explain why it is not directly observed:

- Highest potential energy. It is the maximum on the energy profile, not a minimum. It is not a stable species sitting in a potential well, so it cannot accumulate in any measurable amount.
- Extremely short lifetime. It exists only for roughly one molecular vibration, on the order of 10^{-13} to 10^{-14} s. It is a passing configuration rather than a molecule that can be isolated or held for measurement. (Ultrafast femtosecond spectroscopy

can probe the region near it, but it still does not capture the transition state as a stable species.)

16. Correct Answer is (a)

Partition function;

$Z = e^{-E_0/k_BT} + e^{-E_1/k_BT} + e^{-E_2/k_BT}$

$P_0 = e^{-\frac{E_0}{k_BT}}$

$= e^{-\frac{0}{1.38}\times 10^{-23}}$

$P_0 = 0.919$

$P_1 = e^{-\frac{E_1}{k_BT}}$

$= e^{-1\times\frac{10^{-20}}{1.38}\times 10^{-23}\times 298}$

$P_1 = 0.081$

$P_2 = e^{-E_2/k_BT}$

$= e^{-3\times 10^{-20}/1.38\times 10^{-23}\times 298}$

$P_2 = 0.001$

17. Correct Answer is (b)

The time-dependent Schrodinger equation governs the evolution of wave functions in quantum mechanics and is given by;

$i\hbar\frac{\partial}{\partial t}\,\varphi(x,t) = H\varphi(x,t)$

H is the Hamiltonian operator.

When $\varphi(x,t)$ can be separated into f(t) and g(x). it implies that the wavefunction is in a state of definite energy. It is an eigenstate of the hamoltonian operator. This is the time independent Schrodinger equation.

Therefore, the probability of finding the particle between x and x+dx for such a system is independent of time.

18. Correct Answer is (b)

For a harmonic oscillator, the energy levels are equally spaced at low quantum numbers. Morse potential is a more realistic model than the harmonic oscillator and can be used to describe the **vibrations of molecules** as it accounts for anharmonicity and bond dissociation behavior.

19. Correct Answer is (d)

The Heisenberg uncertainty principle states that the position (x) and momentum (p) operators cannot be known simultaneously with perfect accuracy. Mathematically, this translates to the non-commuting property: [x, p] ≠ 0. However, the statement asks about **commuting**, which means their commutator is **zero**: [x, p] = 0. This is indeed true, signifying the inherent uncertainty principle in quantum mechanics.

20. Correct Answer is (c)

For an ordinary static barrier, the particle's energy is conserved. Tunneling changes the amplitude of the wave function, not the energy. The transmitted particle has the same energy E it had before the barrier, however wide the barrier is. A wider barrier lowers the probability of transmission, but the particles that do get through still carry energy E.

Why the others are true

(A) Inside the barrier the wave function decays exponentially, $\psi \propto E^{-kx}$, with $k = \frac{\sqrt{2}m(V_0-E)}{\hbar}$. A wider barrier means more decay, so the transmitted amplitude is smaller.

(B) The transmission probability goes roughly as $T \approx e^{-2kL}$, and κ grows with barrier height V_o. A higher barrier means a smaller probability of finding the particle on the far side.

(D) After transmission, the wave function picks up a phase shift. In the thick-barrier limit, the transmitted wave has a phase factor of the form e^{iKL} with a length-dependent term, so the phase change is tied to the barrier width. This is the standard textbook treatment, so the statement is accepted as true here.

21. Correct Answer is (a)

Condition for acceptable wave function;

1) function must be continuous

2) finite area

3) single valued

$\psi = \exp(-x)$

$x = 0;\ \varphi = 1;$ Single valued acceptable wavefunction.

22. Correct Answer is (c)

Consider the linear combination vector $X = \sum_k N\ C_k X_k$ where C_k are non-zero scalar coefficients.

To determine whether X is an eigenvector of A we need to check if $AX = \lambda X$ for some scalar λ.

$AX = A(\sum_{k=1}^{N} C_k X_k) = \sum_{k=1}^{N} C_k A X_k$

Using the eigen value equation;

$AX_k = \lambda_k X_k$

$AX = \sum_{k=1}^{N} C_k \lambda_k X_k$

Now, X will be the eigenvector of A if we can express AX in the form λX

CHAPTER-5 KINETICS

PREVIOUS YEAR EXAM QUESTIONS

(TIFR 2010)

1. $N_2O_5\ (g)$ and $NO\ (g)$ react to form NO_2 according to the stoichiometric equation

$N_2O_5\ (g) + NO\ (g) \rightarrow 3NO_2\ (g)$ (R1)

at a given temperature and pressure. A possible mechanism for this overall reaction is:

$N_2O_5 \overset{k_1}{\rightarrow} NO_2 + NO_3$ (M1)

$NO_2 + NO_3 \overset{k_2}{\rightarrow} N_2O_5$ (M2)

$NO_3 + NO \overset{k_3}{\rightarrow} 2NO_2$ (M3)

where NO_3 is an unstable intermediate. What would be the rate expression of the disappearance of N_2O_5 in terms of the concentrations of the stable species and the rate constants given above?

(a) The mechanism given above is not correct since the resultant of the reaction $M1 + M2 + M3$ is not the original reaction R1.

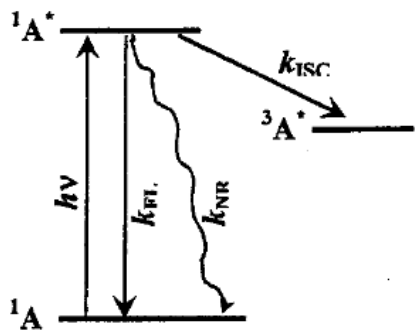
(b) $-\frac{d}{dt}[N_2O_5] = k_1[N_2O_5]\left(1 - \frac{k_2[NO_2]}{k_2[NO_2]+k_3[NO]}\right)$

(c) $-\frac{d}{dt}[N_2O_5] = k_{eff}[N_2O_5][NO]$, where k_{eff} is some function of k_1, k_2, and k_3

(d) $\frac{d}{dt}[N_2O_5] = k_1[N_2O_5]\left(1 + \frac{k_2[NO_2]}{k_2[NO_2]+k_3[NO]}\right)$

(TIFR 2010)

2. An organic molecule A on photoexcitation goes to $^1A^*$. Its various decay channels are shown below. You measure the concentration of $^3A^*$ as a function of time using a fast-response spectrometer, in order to determine the intersystem crossing rate constant k_{ISC}. Assume that the lifetime of $^3A^*$ is very long compared to the other kinetic processes shown there. Which of the following statements would be true for this experiment?



(a) The decay of $^1A^*$ will be multi-exponential.

(b) The formation of $^3A^*$ will be single exponential.

(c) Plotting the concentration of $[^3A^*]$ as a function of time, and fitting it to a single exponential will not give k_{ISC}.

(d) Both (B) and (C) above.

(TIFR 2010)

3. Consider the following reaction carried out in presence of catalyst, C:

$aA + bB \rightarrow dD + eE$

The rate law for this reaction is

$rate = k\,[A]^q[B]^r[C]^s$

Which of the following statements is false?

(a) The exponents q, r and s are often integers.

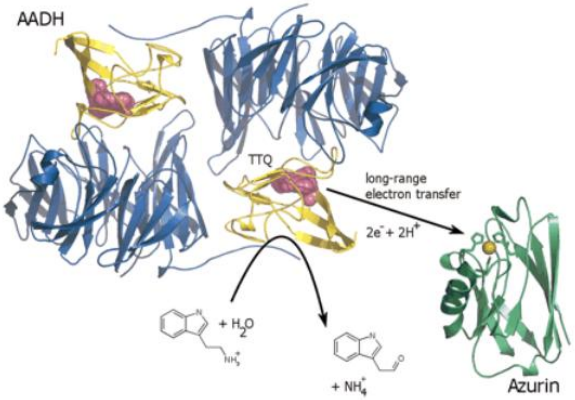
(b) The overall reaction order is $q + r + s$.

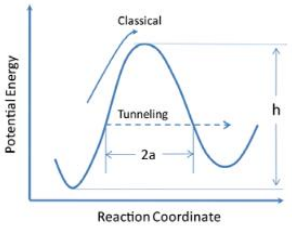
(c) The exponents q and r are always equal to the coefficients a and b, respectively.

(d) The exponents must be determined experimentally.

(TIFR 2011)

4. Proton tunneling process has been implicated to be important part of many enzyme reaction mechanisms like in Aromatic Amine Dehydrogenase (AADH) which does oxidative deamination of substrates to aldehydes via a protein derived Aspartate residue (shown below).





Picture reproduced from Masgrau et al. Science (2006)

Typically in such a reaction, the probability of a tunneling event should depend on:
(a) Only the height (h) of the barrier
(b) Only the width (2a) of the barrier
(c) Both height (h) and width (2a) of the barrier
(d) None of the above

(TIFR 2011)

5. The half-time for a chemical reaction: A → B is 2.3 sec. When a single molecule of A is observed during its conversion to B, what is the predicted time for this conversion to occur?
(a) $e^{-2.3}\ sec$ (b) 4.6 sec
(c) log 2.3 sec (d) undefined

(TIFR 2011)

6. The molar absorption coefficient of a compound in water at 532 nm is $2200\ L\ mol^{-1}cm^{-1}$. When light at that wavelength passes through an aqueous solution of this compound (kept in a 5 cm long cell), 50% of the light was absorbed. What is the concentration of the solution?
(a) $2.7 \times 10^{-5}\ M$ (b) $4.5 \times 10^{-5}\ M$
(c) 1.1 M (d) Insufficient data

(TIFR 2011)

7. The reaction of nitric oxide with ozone takes place according to the following stoichiometry:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The observed rate law for the reaction is found to be

$$-\frac{d[NO]}{dt} = \alpha[O_3]\{[NO] + \beta[NO_2]\}$$

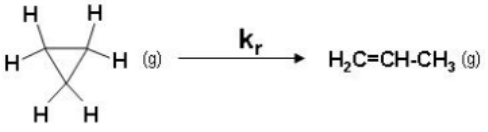
where α and β are constants. To explain the above rate law, the following reaction scheme has been proposed:

$NO + O_3 \overset{k_1}{\rightarrow} NO_2 + O_2$
$NO_2 + O_3 \overset{k_2}{\rightarrow} NO_3 + O_2$
$NO + NO_3 \overset{k_3}{\rightarrow} 2NO_2$

Determine an expression for β.
(a) A unique expression of β cannot be determined from the given information.
(b) k_2/k_1
(c) k_3/k_2
(d) k_1/k_3

(TIFR 2011)

8. For the reaction given below, Activation energy is 271kJ/mol. What is the value of k at 250°C? Note that A (frequency factor) $= 1 \times 10^{-15}\ \text{sec}^{-1}$



(a) $8.568 \times 10^{-12}\ s^{-1}$
(b) $8.568 \times 10^{-1}\ s^{-11}$
(c) $5.141 \times 10^{-11}\ \text{min}^{-1}$
(d) $5.141 \times 10^{-12}\ \text{min}^{-1}$

(TIFR 2012)

9. The molar extinction coefficient (at 550 nm) of compounds A and B are $1 \times 10^4\ M^{-1}\ cm^{-1}$ and $1 \times 10^5\ M^{-1}\ cm^{-1}$ respectively. Solutions of A and B are made at concentrations of $1 \times 10^{-4}\ M$ and $2 \times 10^{-5}\ M$ respectively. In a spectrophotometer set at 550 nm, the percentage of light transmitted by solutions A and B (in two separate experiments) will be:
(a) the same
(b) B will transmit 10 times less light compared to A
(c) B will transmit 5 times less light compared to A
(d) B will transmit 2 times less light compared to A.

(TIFR 2012)

10. The reversible reaction $S \leftrightarrow P$ is catalyzed by a catalyst. The equilibrium constant $K_{eq} = [P]/[S]$ is 2×10^3. The forward rate constant was found to be $5 \times 10^4 sec^{-1}$ and $4 \times 10^{-6}\ \text{sec}^{-1}$ in the presence and in the absence of the catalyst respectively. What is the expected rate constant for the reverse reaction in the absence of the catalyst?
(a) $5 \times 10^8\ sec^{-1}$ (b) $0.8 \times 10^{-10}\ sec^{-1}$
(c) $2 \times 10^{-9} sec^{-1}$ (d) $5 \times 10^{-9}\ sec^{-1}$

(TIFR 2012)

11. A substance A is consumed by a reaction of unknown order. The initial concentration is 1mM, and concentrations at later times are as shown:

Time (min)	[A] (mM)
1	0.83
2	0.72
4	0.56
8	0.38
16	0.24

What is the order of the reaction?
(a) zero (b) first-order
(c) second-order (d) pseudo-first order

(TIFR 2013)

12. The speed of a reaction that involves an enzyme increases as
(a) Temperature decreases
(b) pH becomes less than optimal
(c) Substrate concentration increases
(d) All of the above

(TIFR 2013)

13. The method of initial rates is used to determine the rate law for the reaction given below.

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

The following initial rates were determined at the given partial pressures (p) of reactants.

$p_{NO}(mmHg)$	$p_{H2}(mmHg)$	$Initial\ rate\ (M/min)$
200	400	0.46
400	200	0.92
400	400	1.85

These data imply which of the following rate laws?

(a) Rate $= kp_{NO}p_{H2}$ (b) Rate $= kp_{NO}p_{H2}^2$

(c) Rate $= k\,p_{NO}^2p_{H2}$ (d) Rate $= kp_{NO}^2p_{H2}^2$

(TIFR 2014)

14. What is the de Broglie wavelength of an electron that has been accelerated through a potential difference of 100 V?

(a) 0.123 nm (b) 0.123 Angstrom

(c) 1.23×10^{-11} cm (d) none of the above

(TIFR 2014)

15. For the following chemical reactions

$A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} C$

$B \xrightarrow{k_3} C$

$C \xrightarrow{k_4} B$

The rate constants k_1 and k_2 are at least 1000 times slower than either k_3 or k_4.

During the course of the above reactions the ratio of the products B and C will be

(a) $\frac{[B]}{[C]} = \frac{k_3}{k_4}$ (b) $\frac{[B]}{[C]} = \frac{k_3}{k_4}$

(c) $\frac{[B]}{[C]} = \frac{k_2k_3}{k_1k_4}$ (d) $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

(TIFR 2015)

16. A catalyst:

(a) Participates in the reaction

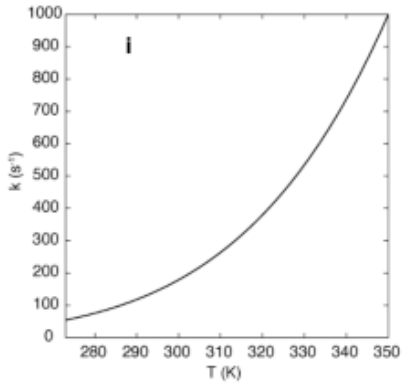
(b) Does not affect a reaction energy path

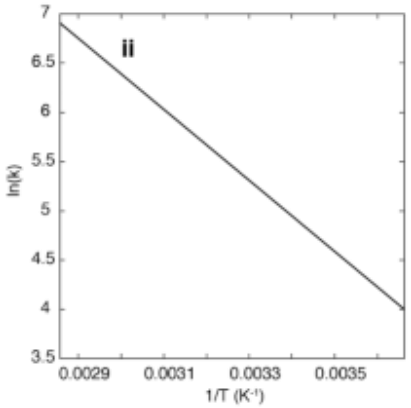
(c) Always decreases the rate for a reaction

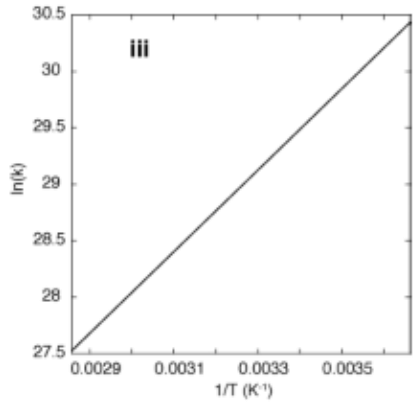
(d) Always increases the activation energy for a reaction

(TIFR 2015)

17. Which of the following plots represent(s) the Arrhenius rate equation, $\mathrm{k = Ae^{-Ea/RT}}$ with $\mathrm{A} = 3 \times 10^7 \mathrm{s}^{-1}$ and $\mathrm{E_a} = 3 \times 10^4$ J/mol.







(a) I (b) ii

(c) iii (d) i and ii

(TIFR 2015)

18. According to the Nernst equation, the potential of an electrode changes by 59.2 mV whenever the ratio of the oxidized and the reduced species changes by a factor of 10 at 25°C. What would be the corresponding change in the electrode potential if the experiment is carried out at 30°C?

(a) 59.2 mV (b) 71.0 mV

(c) 60.2 mV (d) None of the above

(TIFR 2015)

19. Formation of Z from X is theoretically expected to obey the following kinetic scheme.

$$X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Y \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Z$$

age of the universe to reach its native, functional state. However, consider the following simple theoretical model for protein folding:

i) The protein is made up of only 10 amino acids
ii) Each amino acid can exist in one of two states: one correctly and one incorrectly folded
iii) In each second, one amino acid is randomly chosen
iv) If the amino acid is in the incorrectly folded state, it switches to the correctly folded state
v) If the amino acid is in the correctly folded state, nothing happens during that second Starting from all amino acids in the incorrectly folded state, approximately how long will it take on an average for such a protein to fold correctly?

(a) 10 seconds (b) 30 seconds
(c) 30 minutes (d) 30 hours

(TIFR 2026)

43. A species A decays to form B according to a first-order reaction:

$$A \xrightarrow{k} B$$

Assume the initial concentration of A is $[A]_0$ and B is absent initially. (a) The time-dependent growth of species B is proportional to what function of time? (b) How does the time-dependent ratio of concentrations B/A vary as a function of time?

(a) (a) $1 - e^{-kt}$; (b) e^{kt}
(b) (a) $1 - e^{-kt}$; (b) $e^{kt} - 1$
(c) (a) e^{kt} ; (b) $e^{-kt} - 1$
(d) (a) $e^{kt} - 1$; (b) e^{-kt}

(TIFR 2026)

44. Consider a single-step hydrogen atom transfer reaction: $A - H + B \rightarrow A + H - B$. If the rate constant is k_H at a temperature T, then how is the rate constant, typically, going to change if the hydrogen atom is replaced by a deuterium atom? (k_D is the rate constant for the case of deuterium transfer)

(a) $k_D > k_H$
(b) $k_D < k_H$
(c) $k_D = k_H$
(d) cannot be concluded

(TIFR 2026)

45. Which of the following is true when an isolated molecule gets excited to a charge neutral excited state by visible light?

(a) Reduced ionization potential
(b) Increased ionization potential
(c) No change in ionization potential
(d) Zero ionization potential

ANSWER KEY									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(b)	(d)	(c)	(c)	(b)	(b)	(d)	(c)	(b)	(c)
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(c)	(c)	(c)	(a)	(b)	(a)	(d)	(c)	(d)	(d)
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
(a)	(c)	(a)	(c)	(c)	(d)	(c)	(b)	(b)	(c)
31	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
(c)	(b)	(d)	(a)	(d)	(b)	(a)	(c)	(b)	(b)
41	**42**	**43**	**44**	**45**					
(d)	(b)	(b)	(b)	(a)					

SOLUTIONS

1. Correct Answer is (b):

$$-\frac{d}{dt}[N_2O_5] = -k_1[N_2O_5] + k_2[NO_2][NO_3] \ldots\ldots (1)$$

NO_2 is a intermediate .

$$-\frac{d}{dt}[NO_2] = -k_1[N_2O_5] + k_2[NO_2][NO_3] + k_3[NO_3][NO]$$

$$= -k_1[N_2O_5] + k_2[NO_2][NO_3] + k_3[NO_3][NO] = 0$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_2[NO_2] + k_3[NO]}$$

Putting this value in equation (1)

$$-\frac{d}{dt}[N_2O_5] = k_1[N_2O_5] - k_2[NO_2]\frac{k_1[N_2O_5]}{k_2[NO_2] + k_3[NO]}$$

$$= k_1[N_2O_5](1 - \frac{k_2[NO_2]}{k_2[NO_2 + k_3[NO]}$$

2. Correct Answer is (d):

The formation of A^* will likely be single exponential because it is assumed that the lifetime of A^* is much longer compared to the other kinetic processes shown. Therefore the rate of formation of A^* should be dominated by the intersystem crossing process, resulting in a single exponential decay. Plotting the concentration of $3A^*$ as a function of time and fitting it to a single exponential will not give k_{ISC}.

3. Correct Answer is (c):

This statement is false. The exponents in a rate law are determined by the reaction mechanism, not by the overall balanced equation. They match the stoichiometric coefficients only for a true elementary step.

Checking each statement:

(a) True. The orders q, r and s are often integers (0, 1, 2), though fractional and even negative orders do occur in some reactions.
(b) True. The overall reaction order is the sum of the exponents, q + r + s, including the catalyst's order s.
(c) False. For a multistep reaction, the rate law reflects the rate-determining step. For example, $2NO_2 + F_2 \rightarrow 2NO_2F$ has rate = $k[NO_2][F_2]$, not $[NO_2]^2[F_2]$.
(d) True. Rate-law exponents must be found experimentally, for instance by the method of initial rates.

4. Correct Answer is (c):

$T = e^{-2\sqrt{\frac{2m(V-E)}{\hbar^2}}l}$

According to this formula the probability of a tunneling event should depend on both height and width.

5. Correct Answer is (b):

$$t = t_{\frac{1}{2}} \times 2$$
$= 2.3 \times 2$
$= 4.6sec$

6. Correct Answer is (b):

$A = \in bc$
$50\% = 2200Lmol^{-}cm^{-} \times 5cm \times c$
$\frac{50}{100} = 2200Lmol^{-}cm^{-} \times 5cm \times c$
$\frac{50}{100 \times 2200 \times 5} = c$
$c = 4.5 \times 10^{-5}$

7. Correct Answer is (d):

Rate of formation of $[NO_2] = k_1[NO][O_3]$
Rate of consumption of $[NO] = k_3[NO][NO_3]$
Comparing this
$\beta = \frac{k_1}{k_3}$

8. Correct Answer is (c):

Use the Arrhenius equation, $k = A.e^{-E_a/RT}$
Calculation:
T = 250 + 273.15 = 523.15 K
RT = 8.314 × 523.15 ≈ 4349.5 J/mol
E_a/RT = 271,000 / 4349.5 ≈ 62.31
exp(−62.31) ≈ 8.6×10^{-28}
k = $(1 \times 10^{15}\ s^{-1})(8.6 \times 10^{-28}) \approx 8.6 \times 10^{-13}\ s^{-1}$
Converting to minutes: $8.568 \times 10^{-13}\ s^{-1} \times 60$ s/min ≈ $5.141 \times 10^{-11}\ min^{-1}$

9. Correct Answer is (b):

$A = \in bc = -logT$
$-\log T_A = \in_A bC_A$
$= 1 \times 10^4 M^{-}cm^{-}b \times 1 \times 10^{-4}M$
$-logT_A = 1$
$T_A = 10^{-1}$
$\%T_A = 0.1 \times 100 = 10$
$-logT_B = \in_B b \times C_B$
$= 1 \times 10^5 M^{-}cm^{-}b \times 2 \times 10^{-5}$
$-logT_B = 2$
$T_B = 10^{-2}$
$\%T_B = 0.01 \times 100$
$= 1$

It means that B will transmit 10 times less light compared to A.

10. Correct Answer is (c):

$k_{eq} = \frac{k_f}{k_b}$

In the presence of the catalyst

$k_{eq} = \frac{(k_f)_p}{(k_b)_p}$
$(k_b)_p = \frac{(k_f)_p}{k_{eq}}$
$= \frac{5 \times 10^4}{2 \times 10^3}$
$= 25$

In the absence of the catalyst

$k_{eq} = \frac{(k_f)_p}{(k_b)_p}$
$(k_b)_a = \frac{(k_f)_a}{k_{eq}}$
$= \frac{4 \times 10^{-6}}{2 \times 10^3}$
$= 2 \times 10^{-9}s^{-}$

11. Correct Answer is (c):

The reaction is second-order because 1/[A] increases linearly with time.

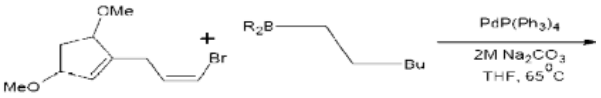
- Second-order test: k = $(1/[A] - 1/[A]_0)/t$ comes out nearly constant at about 0.20 $mM^{-1}min^{-1}$ for every data point.
- First-order test: k = $-\ln([A]/[A]_0)/t$ keeps dropping (0.19 → 0.09), so it fails.
- Zero-order test: the concentration falls fast at first and then slowly, not by a constant amount per minute, so it fails.
- Half-life: the time for the concentration to halve gets longer as [A] drops (about 5 min, then about 10 min), which is the hallmark of second-order kinetics.

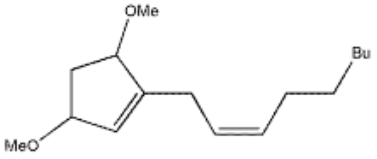
CHAPTER-5 REAGENT'S

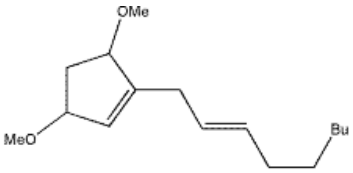
PREVIOUS YEAR EXAM QUESTIONS

(TIFR 2013)

1. What is the result of the following reaction?



(a)


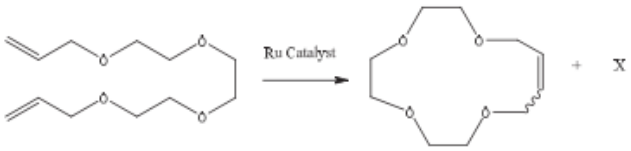
(b)


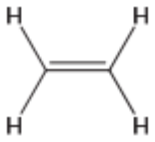
(c) Reaction is unfavourable under given reagents

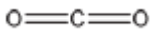
(d) A and B both are plausible

(TIFR 2014)

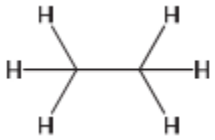
2. What is the side product (X) of the following ring closing metathesis reaction?



(a)


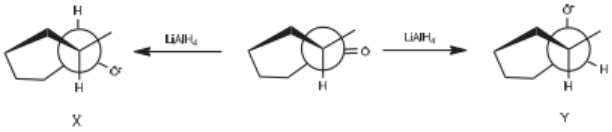
(b)


(c)


(d)


(TIFR 2015)

3. What would be the likely ratio of products X and Y for the following reaction on 2-methyl-cyclohexanone if we consider that torsional effects play a significant role in the reaction outcome?



(a) X: Y = 80: 20

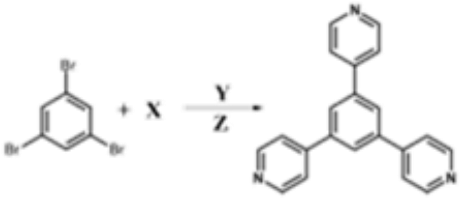
(b) X: Y = 50: 50

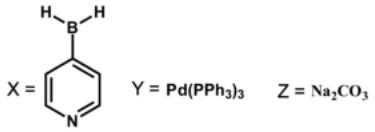
(c) X: Y = 20: 80

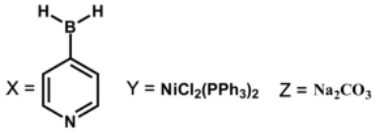
(d) X: Y = 1: 99

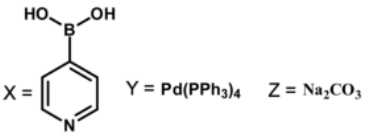
(TIFR 2015)

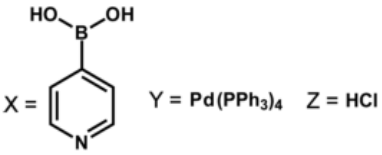
4. Degenerate $C-C$ coupling reactions are very important for synthesizing supramolecular organic structures. Name the reagents X, Y and Z that would be necessary to make the C_3 symmetric product?



(a)


(b)


(c)


(d)


(TIFR 2017)

5. What are the products of the following reaction?



(a) $H_2 + Et_3N + LiCl + AlH_3$

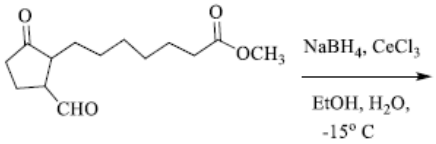
(b) $LiH + Et_3N + HCl + 0.5Al_2H_6$

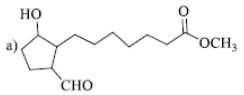
(c) $LiCl + H_3Al{:}\,NEt_3 + H_2$

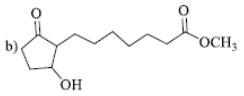
(d) $LiCl + NEt_3 + H_2 + 0.5\,Al_2H_6$

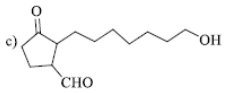
(TIFR 2019)

6. Predict the product obtained in the following reaction





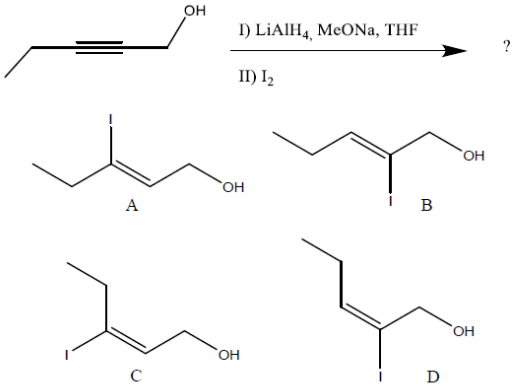




d) all of these.

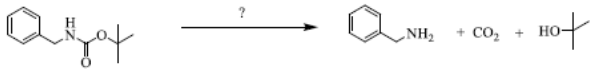
(TIFR 2019)

7. What is the main product of below reaction?



(TIFR 2020)

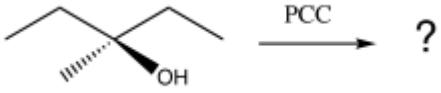
8. Predict the reagent for the following amine de-protection reaction



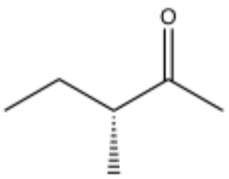
(a) H_3O^+/H_2O (b) $NaOH/H_2O$
(c) $NaCl/H_2O$ (d) $Pd/C,H_2$

(TIFR 2021)

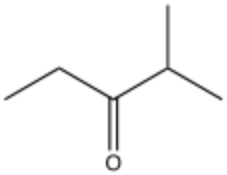
9. Predict the product of the following reaction [PCC = Pyridinium chlorochromate].



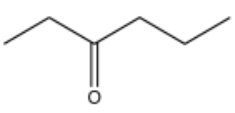
(a)



(b)



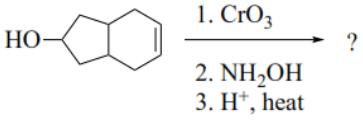
(c)



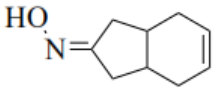
(d) No reaction

(TIFR 2022)

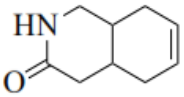
10. Predict the product.



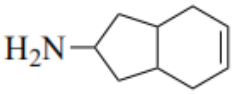
(a)



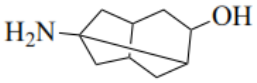
(b)



(c)

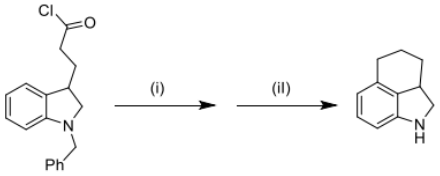


(d)



(TIFR 2024)

11. Predict the reagents (i) and (ii) for the following two-step reaction.



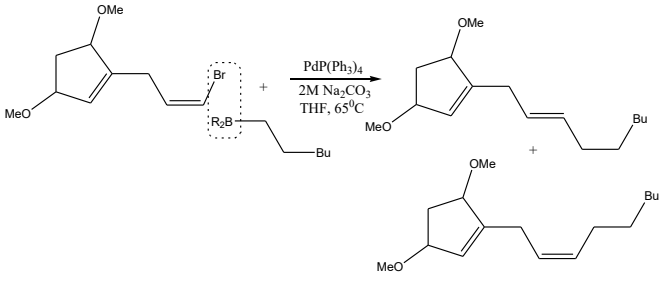
(a) (i) NaOH; (ii) Pd/C, H_2 (5 bar)
(b) (i) Pd/C, H_2 (5 bar); (ii) AlCl3
(c) (i) $AlCl_3$; (ii) Pd/C, H_2 (5 bar)
(d) (i) Pd/C, H_2 (5 bar); (ii) NaOH

ANSWER KEY									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(d)	(a)	(a)	(c)	(c)	(a)	(a)	(a)	(d)	(b)
11									
(c)									

SOLUTIONS

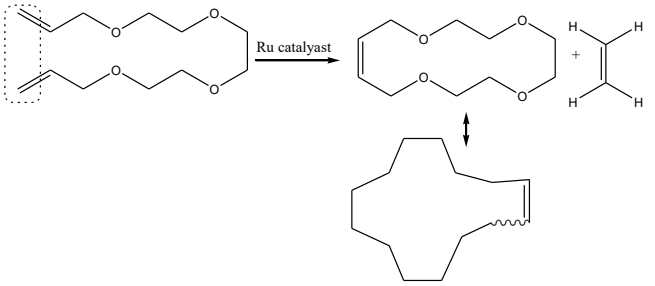
1. Correct Answer is (d)

With the increase in the amount of the base, the concentrations of the two borates gradually become similar, hence both product obtained



2. Correct Answer is (a)

This is metathesis reaction in which alkene is byproduct, as shown below



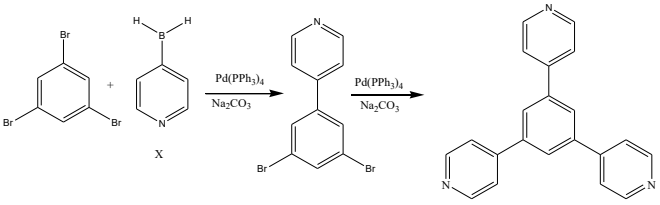
3. Correct Answer is (a)

$LiAlH_4$ is a small hydride donor, so steric hindrance is not the deciding factor. Torsional strain is, as the question says.

- Axial attack (the hydride comes in parallel to the axial C-H bonds at C3 and C5) lets the forming C-H bond stay staggered relative to the adjacent C2-C3 and C6-C5 bonds, so there is little torsional strain in the transition state. This path is favored and gives the equatorial alkoxide, which is trans-2-methylcyclohexanol.
- Equatorial attack makes the incoming hydride pass close to the axial hydrogens on C2 and C6, which causes eclipsing (torsional) strain in the transition state. It gives the axial alkoxide (cis isomer) as the minor product.

  The experimental result for 2-methylcyclohexanone with $LiAlH_4$ is roughly 75-80% axial attack and 20-25% equatorial attack, which matches 80:20. Attack on the less hindered face is therefore preferred, but not exclusively, so the ratio is not 1:99.

4. Correct Answer is (c)



5. Correct Answer is (c)

Et_3NHCl is the hydrochloride salt of triethylamine, so the N-H^+ proton is acidic and Cl^- is the counter-ion. $LiAlH_4$ supplies hydride, so the reaction goes as follows:

1. **Acid-base step:** H^- (from AlH_4^-) combines with the acidic N-H proton of Et_3NH^+ to give **H_2**.
2. **Chloride exchange:** Li^+ pairs with Cl^- to precipitate **LiCl**, which is insoluble in toluene and drives the reaction forward.
3. **Alane formation:** The remaining AlH_3 is a Lewis acid, and the freed Et_3N is a Lewis base, so they combine into the stable adduct **$H_3Al{\cdot}NEt_3$** (trimethylamine alane analogue).

   Overall:

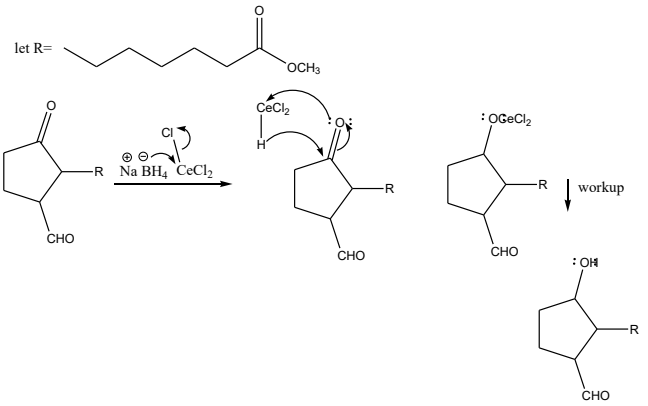
   $LiAlH_4 + Et_3NHCl \rightarrow LiCl + H_3Al{\cdot}NEt_3 + H_2$

   This is a standard laboratory route to amine-alane complexes. The other options fail for these reasons:

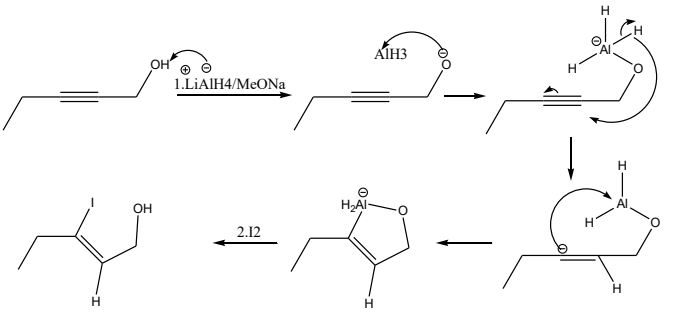
- **A and D** show free AlH_3 or Al_2H_6 alongside free Et_3N, but AlH_3 is electron-deficient and would not stay uncomplexed in the presence of a Lewis base like Et_3N.
- **B** forms LiH and HCl, which is not reasonable. HCl would immediately react with any hydride present and cannot coexist with it.

6. Correct Answer is (a)

Luche's reagent selectively reduce carbonyl ketone to alcohol.

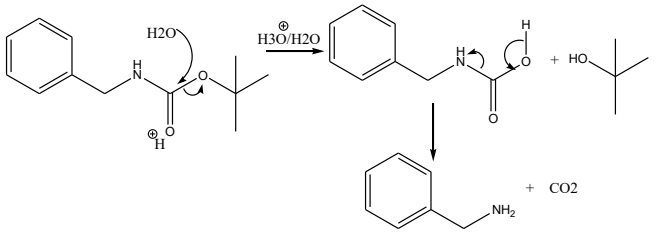


7. Correct Answer is (a)



8. Correct Answer is (a)

Acidic hydrolysis only can give following reaction.

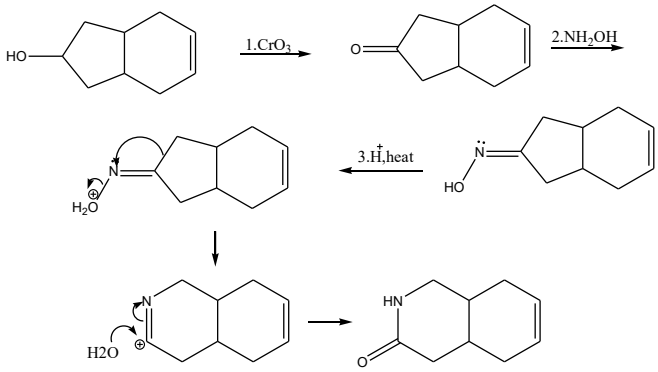


9. Correct Answer is (d)

In a tertiary alcohol, the carbon atom bonded to the hydroxyl group (OH) already has three other attached carbon atoms. This means there are no more hydrogen atoms on the carbon to be removed by PCC, **PCC cannot oxidize tertiary alcohols.** hence no reaction

10. Correct Answer is (b)

Secondary alcohol on oxidation by CrO3 gives ketone,



11. Correct Answer is (c)

Step (i): $AlCl_3$. The acid chloride side chain on C3 of the N-benzylindoline reacts with $AlCl_3$ to form an acylium ion. This attacks the aromatic ring at C4 (the position peri to the C3 substituent) in an intramolecular **Friedel-Crafts acylation**. The result is a new six-membered ring, giving a tricyclic ketone. The N-benzylindoline nitrogen is an electron-donating aniline-type nitrogen, which activates the ring, though it is para to C5 and C7, not C4, so the cyclization is driven mainly by the favorable ring size.

Step (ii): Pd/C, H_2 (5 bar). This does two things in one step:

- It **hydrogenolyzes the N-benzyl group**, removing Ph-CH_2 as toluene and leaving the free N-H indoline, as seen in the product.
- It **reduces the benzylic aryl ketone to CH_2**. Aryl ketones undergo hydrogenolysis over Pd/C because the C-O bond is benzylic, giving the saturated six-membered ring in the product.

Why the order matters:

- **Friedel-Crafts must come first.** If H_2/Pd-C were run first, the acid chloride would be reduced or the N-benzyl group lost, and a free N-H amine would then complex with $AlCl_3$ (or be acylated), shutting down the cyclization. Options B and D therefore fail.
- **NaOH (options A and D)** would simply hydrolyze the acid chloride to the carboxylic acid and could not cyclize it.

