

ENTRANCE EXAMINATIONS – 2018
(Ph.D. Admissions - January 2019 Session)

Ph.D. Chemistry

TIME: 2 HOURS

MAXIMUM MARKS: 80

HALL TICKET NUMBER:

INSTRUCTIONS

1. Write your **HALL TICKET NUMBER** in the space provided above and also on the **OMR ANSWER SHEET** given to you.
2. Make sure that pages numbered from **1 - 19** are present (excluding 4 pages assigned for rough work).
3. There are eighty (80) multiple choice questions in this paper (20 in Part-A and 60 in Part-B); each question carries two (2) marks.
4. Attempt **all questions** in Part-A ($20 \times 2 = 40$ marks), and **any 20** in Part-B ($20 \times 2 = 40$ marks); if more questions are answered in Part-B, only the **first 20** will be considered for grading.
5. **There is negative marking** for both Part-A and Part-B. **Each wrong answer carries - 0.66 mark.**
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Hand over the OMR answer sheet to the invigilator at the end of the examination.
8. **In case of a tie**, the marks obtained in **Part-A** will be used to determine the order of merit.
9. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
10. Calculators are allowed. Cell phones are not allowed.
11. Useful constants are provided at the beginning of Part-A in the question paper.
12. OMR sheets without hall ticket number will not be evaluated and the University shall not be held responsible.

Useful Constants:

Rydberg constant = 109737 cm^{-1} ; Faraday constant = $96500 \text{ C} = 23.06 \text{ kcal/V}$; Planck constant = $6.625 \times 10^{-34} \text{ J s}$; Boltzmann constant = $1.380 \times 10^{-23} \text{ J K}^{-1}$; Gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$; Mass of electron = $9.109 \times 10^{-31} \text{ kg}$; Mass of proton = $1.672 \times 10^{-27} \text{ kg}$; Charge of electron = $1.6 \times 10^{-19} \text{ C}$; 1 bar = 10^5 N m^{-2} ; RT/F (at 298.15 K) = 0.0257 V ; Avogadro number = 6.022×10^{23} ; Speed of light = $3.0 \times 10^8 \text{ m s}^{-1}$

Part-A

- Diborane combines with excess NH_3 at high temperature to form

[A] $\text{H}_3\text{B} \leftarrow \text{NH}_3$	[B] $\text{B}_3\text{N}_3\text{H}_6$
[C] $\text{H}_3\text{B} \rightarrow \text{NH}_3$	[D] $(\text{BN})_n$
- The increasing order of polarizing powers of Na^+ , Mg^{2+} and Al^{3+} ions is

[A] $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$	[B] $\text{Na}^+ < \text{Al}^{3+} < \text{Mg}^{2+}$
[C] $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$	[D] $\text{Mg}^{2+} < \text{Na}^+ < \text{Al}^{3+}$
- If BH_3^- is isolobal with $[\text{M}(\text{CO})_5]^+$, the 3d transition metal M is

[A] Cr	[B] Mn
[C] Fe	[D] Co
- N_2 ligand in $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)\text{Ru}(\text{NH}_3)_5]^{4+}$ complex is in

[A] infrared active end-on-bridge mode
[B] Raman active end-on-bridge mode
[C] infrared active side-on-bridge mode
[D] Raman active side-on-bridge mode
- The total number of metal-metal bonds present in $(\eta^4\text{-C}_4\text{H}_4)_2\text{Fe}_2(\text{CO})_3$ and $\text{Co}_4(\text{CO})_{12}$ are respectively,

[A] 3 and 2	[B] 4 and 3
[C] 3 and 6	[D] 4 and 6

6. Photosynthesis by plants involves two major events, namely, visible light absorption and catalytic water oxidation. The specific metal ions engaged in the above two events are respectively,

[A] Mg and Co

[B] Mg and Mn

[C] Mn and Mg

[D] Mn and Fe

7. Reaction of hydrocinnamic acid ($\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$) with trifluoroacetic anhydride provides

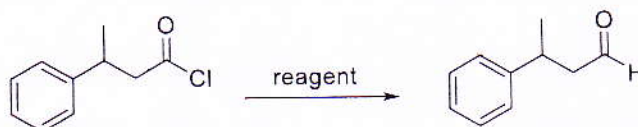
[A] hydrocinnamic anhydride

[B] indan-1-one

[C] ethylbenzene

[D] mixed anhydride of hydrocinnamic acid and trifluoroacetic acid

8. The appropriate reagent to carry out the following transformation is



[A] NaBH_4

[B] $\text{LiAlH}(\text{O}-t\text{-Bu})_3$

[C] LiAlH_4

[D] NaH

9. The precipitate formed in the estimation of glucose by its reaction with Fehling's solution is

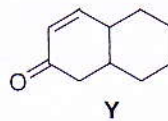
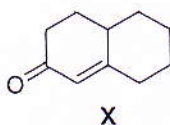
[A] CuO

[B] CuCO_3

[C] $\text{Cu}(\text{OH})_2$

[D] Cu_2O

10. The predicted electronic absorption maxima of **X** and **Y** are respectively,



[A] 239 nm and 245 nm

[B] 244 nm and 245 nm

[C] 239 nm and 227 nm

[D] 244 nm and 227 nm

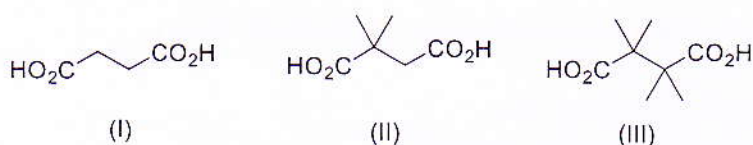
11. According to Hammond's postulate, structure of the transition states for exothermic and endothermic reactions resemble the structure(s) of

- [A] reactant
- [B] product
- [C] reactant and product respectively
- [D] product and reactant respectively

12. Given that there are 20 amino acids, the number of possible tripeptides are

- [A] 8000
- [B] 1200
- [C] 400
- [D] 6400

13. The order of increasing reaction rates for cyclic anhydride formation from the following succinic acids is



- [A] (I) < (III) < (II)
- [B] (I) < (II) < (III)
- [C] (III) < (II) < (I)
- [D] (II) < (III) < (I)

14. The free energy change in a process is affected by

- [A] the entropy change of the system and the surrounding
- [B] only the entropy change of the system
- [C] only the entropy change of the surrounding
- [D] only the enthalpy change of the system

15. From the Hückel molecular orbitals, one can deduce that the spin density in allyl radical is predominantly localized on

- [A] atoms 1 and 2
- [B] atom 2
- [C] atoms 1 and 3
- [D] all the atoms equally

16. In the photoelectric experiment, slope of the kinetic energy vs frequency plot is
- [A] Planck constant [B] Avogadro number
[C] velocity of electron [D] work function
17. Variance and standard deviation (σ) are two ways to report statistical error. Which of the following correctly describes the relationship between variance and standard deviation?
- [A] variance = σ [B] variance = $\sqrt{\sigma}$
[C] variance = σ^2 [D] variance = $\sqrt[4]{\sigma}$
18. Which, among the following, is a set of linearly independent functions?
- [A] $\sin^2 x, \cos^2 y, 1$ [B] $8, x, x^2, 3x^2 - 1$
[C] $\sin x, \cos x, e^{ix}$ [D] $\sin^2 x, \cos^2 x, 1$
19. According to Graham's law of effusion, the rate of effusion is
- [A] independent of molar mass
[B] directly proportional to molar mass
[C] inversely proportional to square root of molar mass
[D] inversely proportional to square of molar mass
20. A phase transition occurs at the temperature at which the system in the two phases have the same
- [A] internal energies [B] entropies
[C] volumes [D] chemical potentials

Part-B

21. A sample of pure Na_2CO_3 weighing 0.3542 g is dissolved in water and titrated with a solution of HCl. A volume of 30.23 mL of aqueous HCl solution is required to reach the end point. The molarity of acid is close to (atomic weight of Na = 23)

[A] 0.055 M

[B] 0.11 M

[C] 0.22 M

[D] 2.2×10^4 M

22. A sample of 5.0 mmol of iron(II) sulfate is dissolved in 100 mL of aqueous sulfuric acid and titrated with 0.10 M cerium(IV) sulfate solution. The potential of the inert electrode (E in V) in the solution at 25°C , after the addition of 10 mL and 60 mL of Ce(IV) solution are respectively, [Given: $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$; $E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V}$]

[A] 0.77 and 1.61

[B] 0.24 and 0.24

[C] 0.81 and 1.65

[D] 0.73 and 1.57

23. Iron in a 0.70 g sample that contains 25% Fe_2O_3 is precipitated as $\text{Fe}(\text{OH})_3$ using aqueous ammonia solution. The volume of aqueous ammonia solution of 2.3% (w/v) required to complete the precipitation of iron is (atomic weight of Fe = 55.85)

[A] 4.89 mL

[B] 1.69 mL

[C] 2.46 mL

[D] 1.23 mL

24. The correct statement(s) about crown ethers among the following is/are

- (i) They are soluble in both organic solvents and water
- (ii) They are soluble only in organic solvents
- (iii) They are soluble only in water
- (iv) They are structurally flexible

[A] (i) and (iv)

[B] (iii) and (iv)

[C] (i)

[D] (ii) and (iv)

25. The crystal field stabilization energy (CFSE) of $[\text{Co}(\text{CN})_6]^{3-}$ is

[A] $-24Dq$ [B] $-4Dq + P$ [C] $-24Dq + 3P$ [D] $-24Dq + 2P$

26. Among the following configurations in octahedral crystal field, the configuration expected to have higher than spin-only magnetic moment is

- [A] d^3 (in both weak and strong ligand fields) [B] d^4 (in weak ligand field)
 [C] d^4 (in strong ligand field) [D] d^5 (in weak ligand field)

27. According to HSAB theory the equilibrium constants (K) of the following two reactions $\text{CdI}_2 + \text{CaF}_2 \rightleftharpoons \text{CdF}_2 + \text{CaI}_2$ and $\text{AlI}_3 + 3\text{NaF} \rightleftharpoons \text{AlF}_3 + 3\text{NaI}$ are expected to be

- [A] > 1 and < 1 , respectively [B] < 1 and > 1 , respectively
 [C] > 1 in both cases [D] < 1 in both cases

28. The standard potentials (E^0) for $\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$ and $[\text{Ag}(\text{CN})_2]^- + e^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$ are 0.80 and -0.31 V, respectively. The formation constant of the complex $[\text{Ag}(\text{CN})_2]^-$ at 25°C is close to

- [A] 4.5×10^{18} [B] 1.7×10^8
 [C] 2.24×10^{-19} [D] 1.7×10^{-8}

29. The reasons for the observation of AA'XX' spectral pattern at -19°C and a broad single peak at 67°C for ethylenic protons in the ^1H NMR (60 MHz) spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ are

- (i) static and dynamic structures of the compound at -19°C and 67°C , respectively.
 (ii) rotation of the olefin about the metal-olefin bond axis.
 (iii) exchange of C_2H_4 between two different molecules.

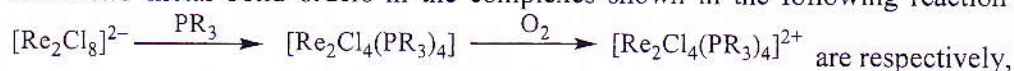
- [A] (i), (ii) and (iii) [B] (i) and (ii)
 [C] (i) and (iii) [D] (ii) and (iii)

30. The order of increasing metal-carbon bond distances in the following compounds is

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$	$(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$	$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$
I	II	III

- [A] $\text{I} < \text{II} < \text{III}$ [B] $\text{II} < \text{I} < \text{III}$
 [C] $\text{III} < \text{II} < \text{I}$ [D] $\text{I} < \text{III} < \text{II}$

31. The metal-metal bond orders in the complexes shown in the following reaction sequence



are respectively,

[A] 4, 3 and 4

[B] 4, 3 and 2

[C] 2, 3 and 4

[D] 3, 4 and 3

32. The number of lines expected in the electron paramagnetic resonance (epr) spectrum of $^{63}\text{Cu}^{2+}$ ion at room temperature (25°C) is

[A] 0

[B] 2

[C] 3

[D] 4

33. Choose the correct statement(s) in connection with the structure of $\text{Fe}(\text{CO})_5$ molecule.

(i) The IR spectrum is consistent with a trigonal bipyramidal structure with distinct axial and equatorial CO groups.

(ii) The Raman spectrum is consistent with a trigonal bipyramidal structure with distinct axial and equatorial CO groups.

(iii) The room temperature (25°C) ^{13}C NMR spectrum clearly shows that it has a trigonal bipyramidal structure with distinct axial and equatorial CO groups.

[A] (i) and (ii)

[B] (ii) and (iii)

[C] (i) and (iii)

[D] (i) only

34. Choose the compound(s) that is(are) hypervalent among the following:

AsCl_3 , SbF_5 , $\text{S}(\text{O})\text{Cl}_2$, $[\text{Ph}_4\text{P}]^+[\text{Cl}]^-$

[A] SbF_5 and $\text{S}(\text{O})\text{Cl}_2$

[B] SbF_5 only

[C] AsCl_3 and SbF_5

[D] SbF_5 , $\text{S}(\text{O})\text{Cl}_2$ and $[\text{Ph}_4\text{P}]^+[\text{Cl}]^-$

35. The total number of microstates possible for a d^3 ion and a ^2P term are respectively,

[A] 120 and 6

[B] 45 and 3

[C] 60 and 4

[D] 80 and 5

36. The effective magnetic moment taking spin-orbit coupling into account for $[\text{Ni}(\text{en})_3]^{2+}$ considering the following parameters, $\alpha = 4$, $\lambda = -315 \text{ cm}^{-1}$ and $\Delta_0 = 11500 \text{ cm}^{-1}$ is

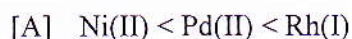
[A] 3.14 BM

[B] 2.83 BM

[C] 2.14 BM

[D] 4.83 BM

37. The lability of the square planar complexes, assuming an associative mechanism for substitution, is in the order



38. Consider the following equation: $\text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$. Choose the correct statements from the following

(i) The potential for this reaction increases with the increase in pH

(ii) The potential for this reaction decreases with the increase in pH

(iii) The potential for this reaction increases with the increase in the concentration of $[\text{Fe}]^{2+}$

(iv) The potential for this reaction decreases with the increase in the concentration of $[\text{Fe}]^{2+}$

[A] (i) and (iii)

[B] (ii) and (iii)

[C] (ii) and (iv)

[D] (i) and (iv)

39. The correct matching of the items in the following table are

1.	Fischer Tropsch process	a.	HCo(CO)_4
2.	water gas shift reaction	b.	$\text{Os}_3(\text{CO})_{10}(\text{CH}_4)$
3.	oxo process	c.	carbide/carbine mechanism
4.	agostic Interaction	d.	$\text{Ru(bpy)}_2\text{Cl}_2$

[A] 1=c; 2=d; 3=a; 4=b

[B] 1=c; 2=a; 3=d; 4=b

[C] 1=d; 2=c; 3=b; 4=a

[D] 1=a; 2=d; 3=b; 4=c

40. The ground state term symbol representation and magnetic moment for Pr^{3+} ion ($4f^2$) are respectively,

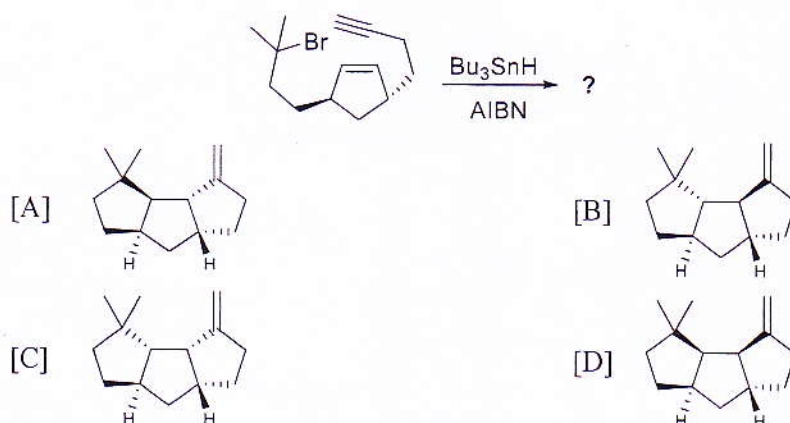
[A] $^3\text{H}_4$ and 3.58 BM

[B] $^4\text{I}_{9/2}$ and 2.68 BM

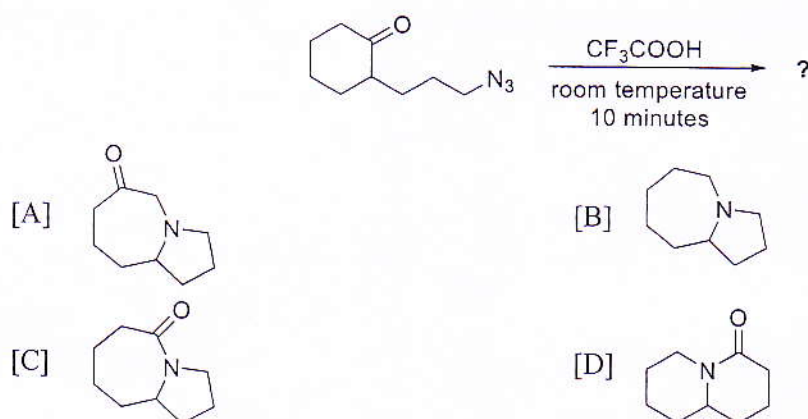
[C] $^2\text{F}_{5/2}$ and 2.54 BM

[D] $^3\text{H}_6$ and 2.82 BM

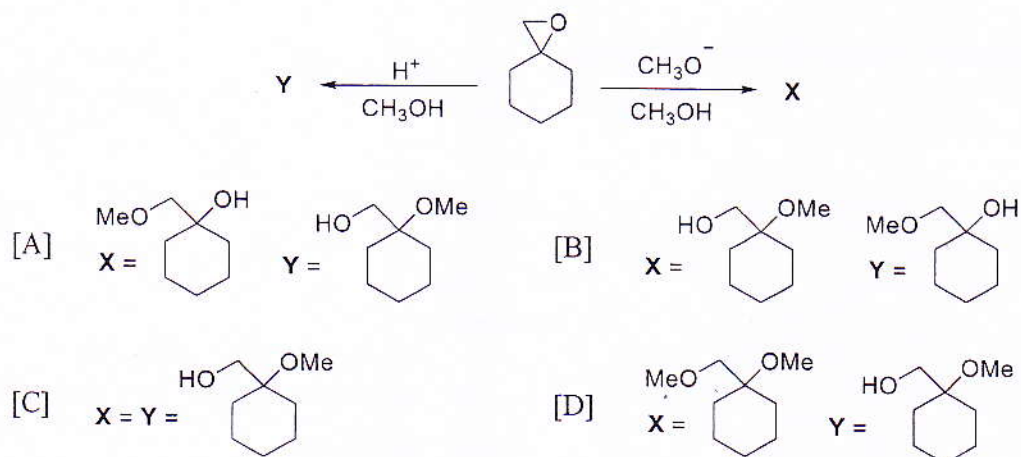
41. The major product formed in the following transformation is



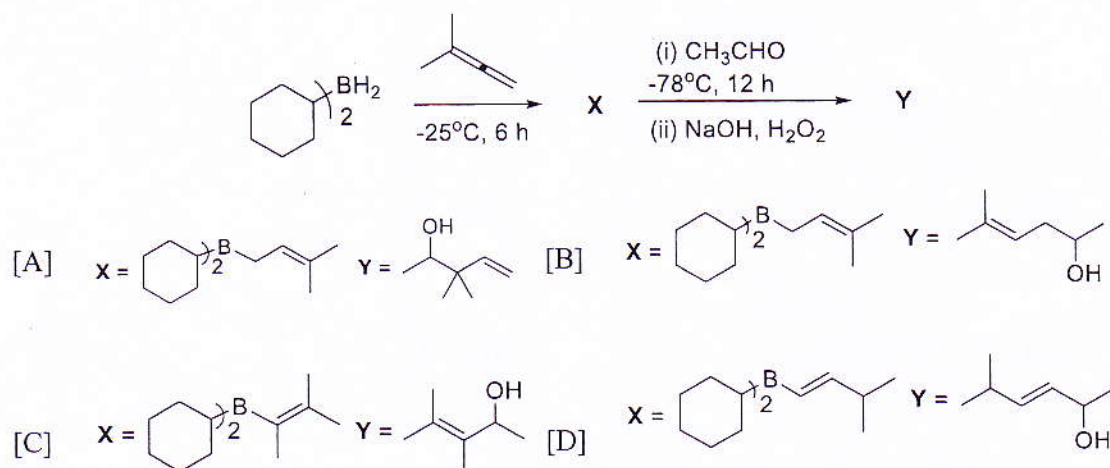
42. The major product formed in the following reaction is



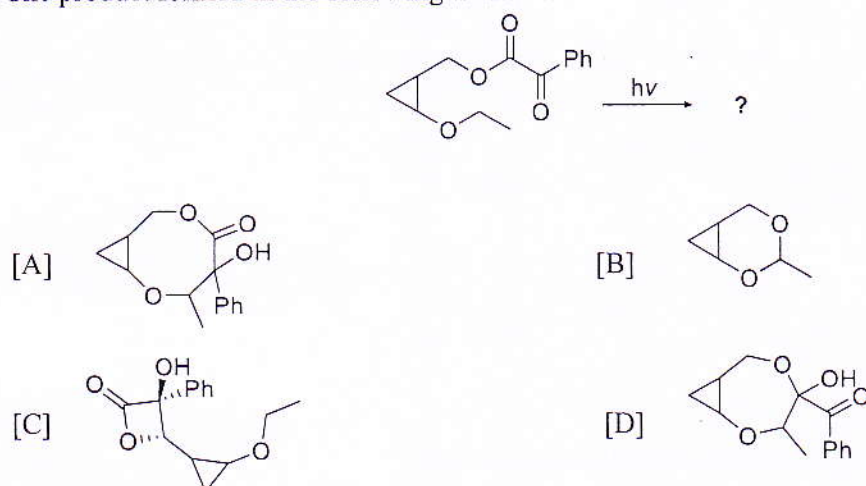
43. Identify the products **X** and **Y** in the following reactions.



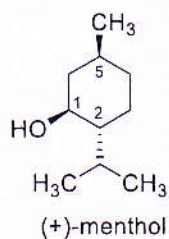
44. Identify X and Y in the following reaction sequence.



45. The product formed in the following transformation is



46. The absolute configuration of (+)-menthol is



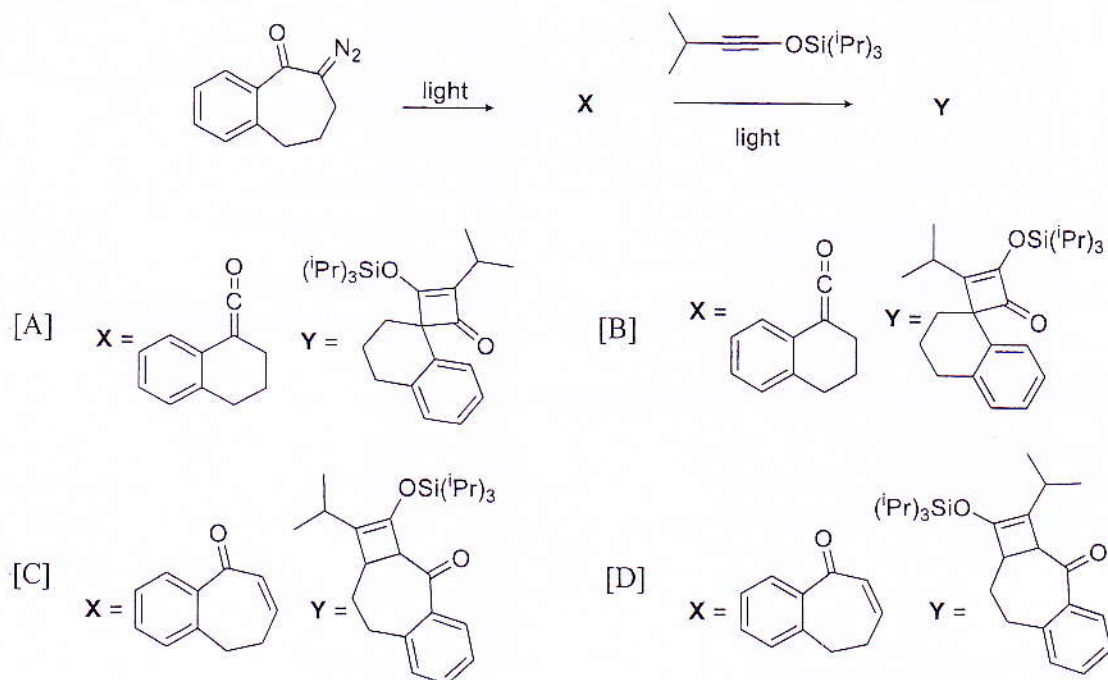
[A] 1S, 2S, 5S

[B] 1S, 2R, 5S

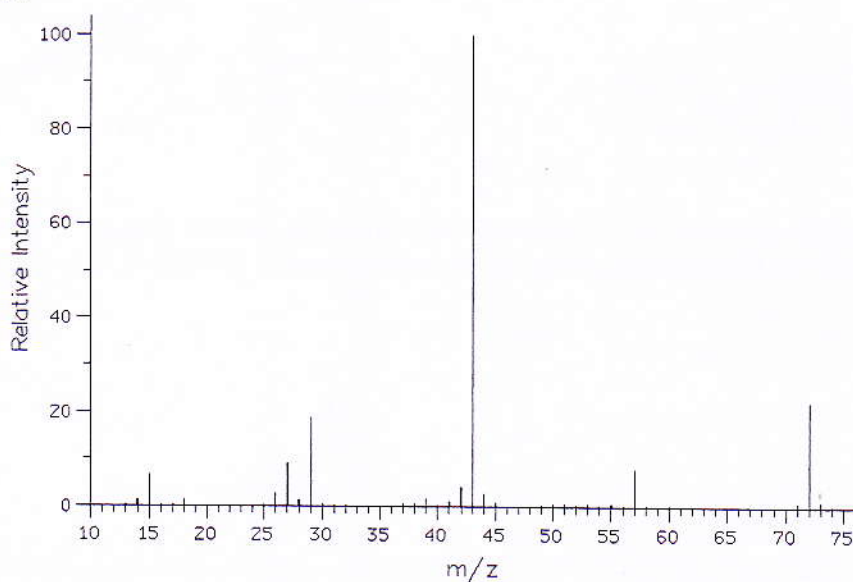
[C] 1S, 2S, 5R

[D] 1S, 2R, 5R

47. Identify the products **X** and **Y** in the following transformation.



48. The mass spectrum of a compound with molecular formula $\text{C}_4\text{H}_8\text{O}$ is given below. The compound is



[A] butyraldehyde

[B] butan-2-one

[C] tetrahydrofuran

[D] cyclobutanol

49. Predict the most appropriate products **X** and **Y** in the following reactions.



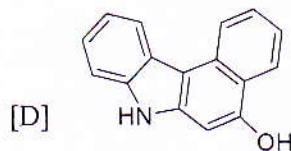
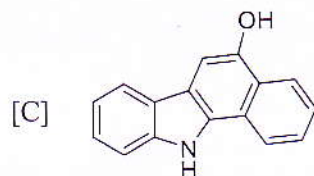
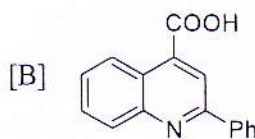
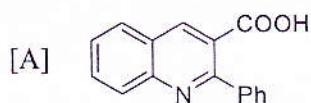
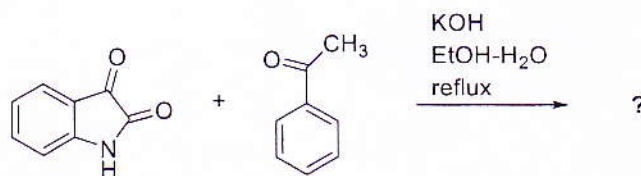
[A] **X** = RCH_2COOH
Y = cyclohexanone

[B] **X** = RCOOMe
Y = cyclohexanone

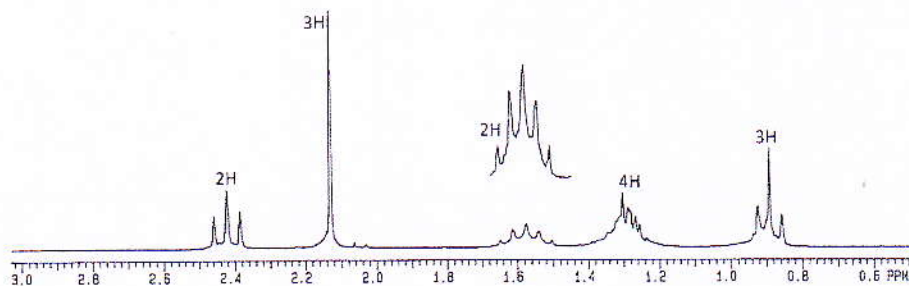
[C] **X** = RCOOMe
Y = 2-methylcyclopentanone

[D] **X** = RCH_2COOH
Y = 1-methylcyclopentanol

50. The product obtained in the following reaction is



51. The ^1H -NMR spectrum of a compound with molecular formula $\text{C}_7\text{H}_{14}\text{O}$ is given below. The IR spectrum of the same compound has an intense band at 1718 cm^{-1} . The compound is



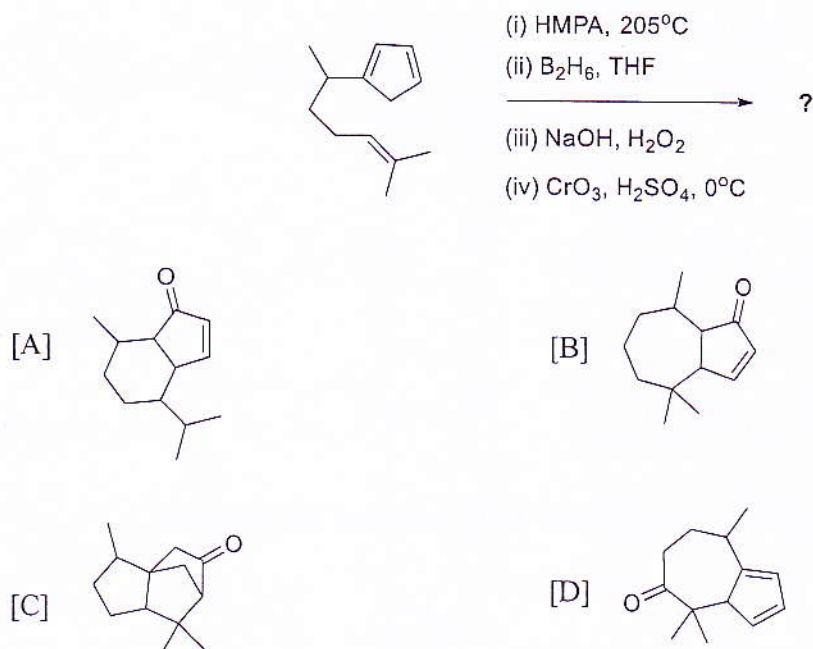
[A] 3-heptanone

[B] 3-methyl-2-hexanone

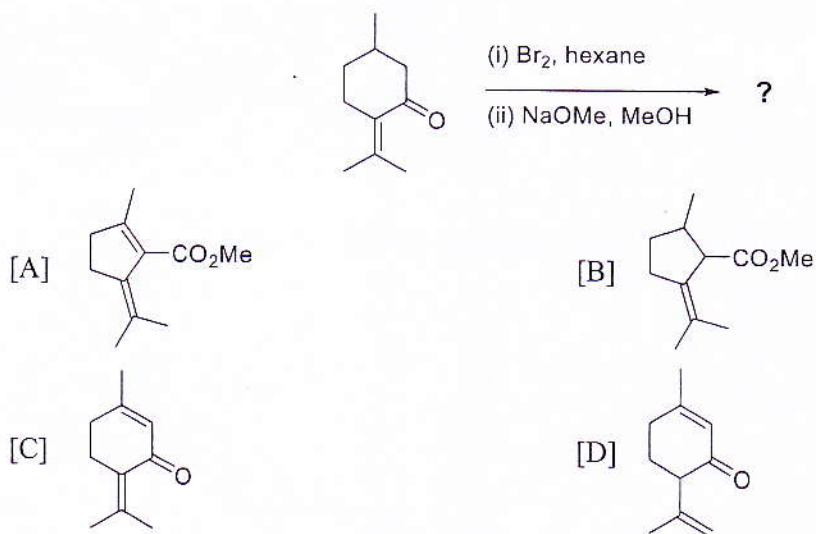
[C] 2-heptanone

[D] 4-methyl-2-hexanone

52. The product obtained in the following reaction is



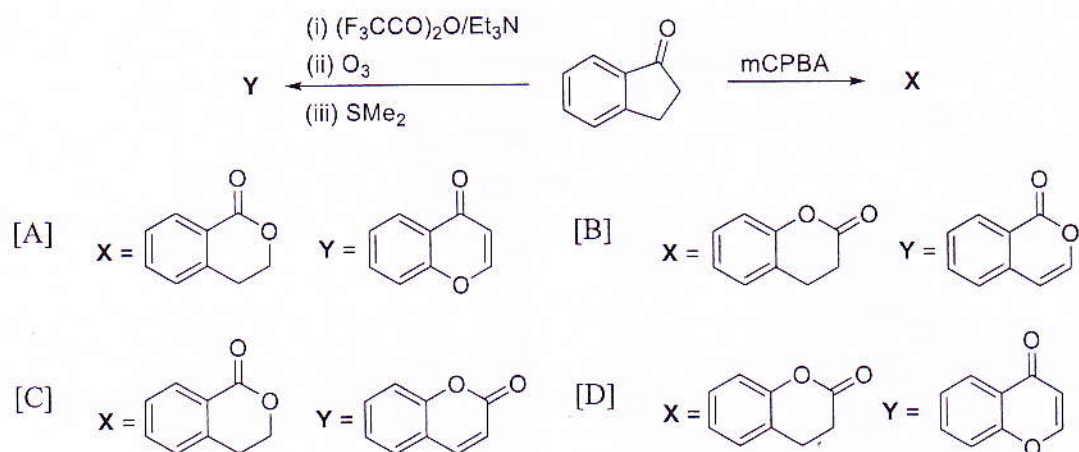
53. The major product formed in the following reaction is



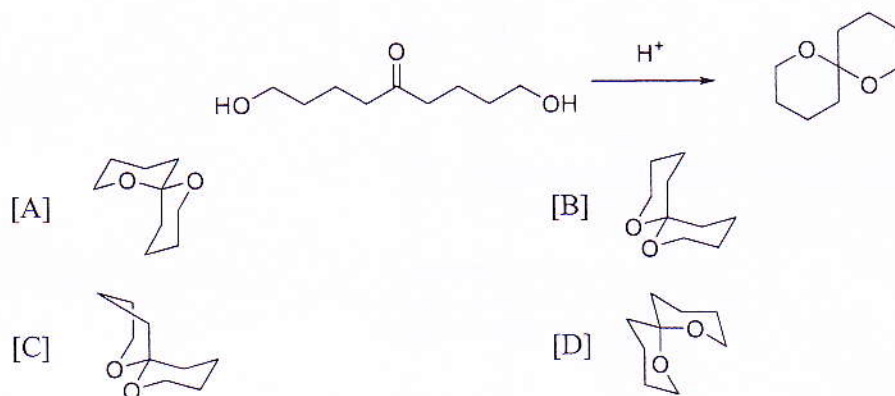
54. The side product obtained in the Reimer-Tiemann reaction of indole via cyclopropanation is

- | | |
|--------------------------------------|--------------------------------------|
| [A] 3-chloroquinoline | [B] 2-chloroquinoline |
| [C] 2-chloro indole-3-carboxaldehyde | [D] 3-chloro indole-2-carboxaldehyde |

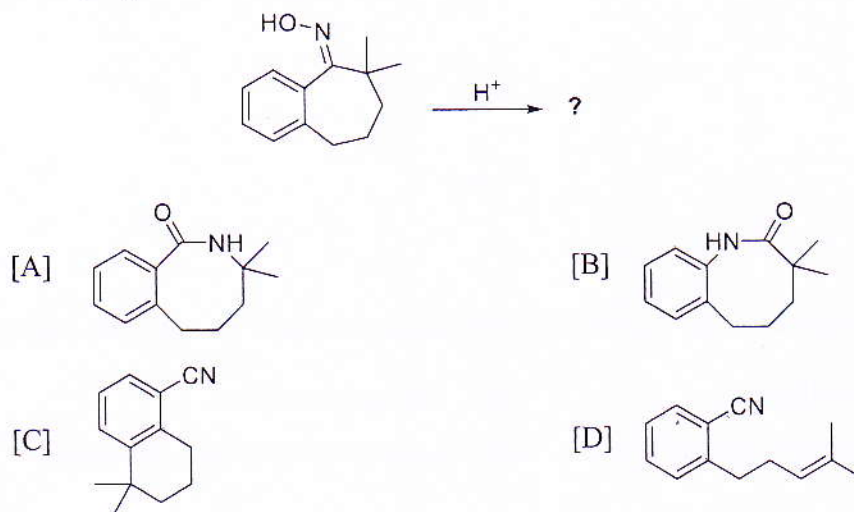
55. Identify **X** and **Y** in the following conversions.



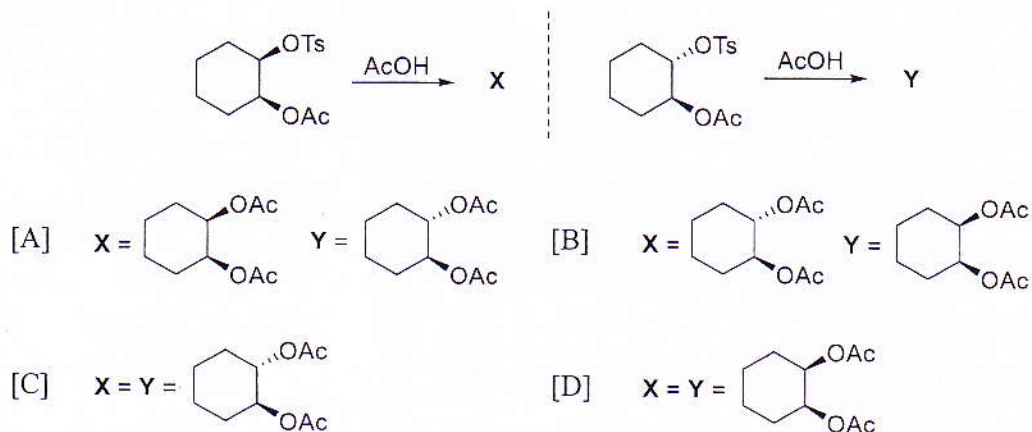
56. The most favorable conformer of the product in the following transformation is



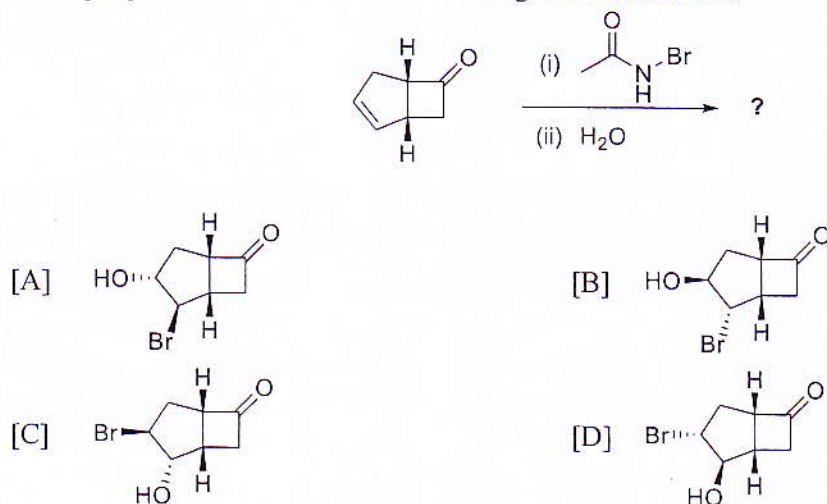
57. The major product formed in the following transformation is



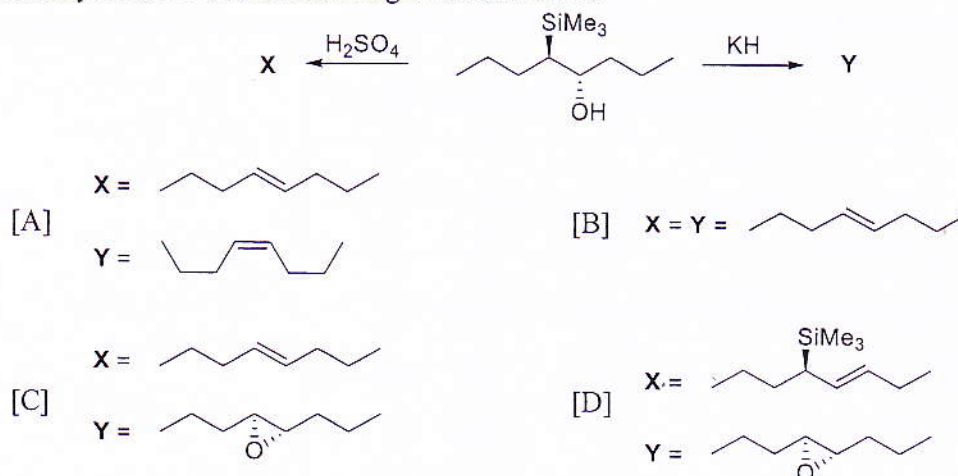
58. Identify X and Y in the following transformations



59. The major product obtained in the following transformation is



60. Identify X and Y in the following transformations.



61. The fraction of light transmitted through a 200 mm thick glass plate is 0.955. The absorption coefficient of the glass is

[A] $2.0 \times 10^{-4} \text{ mm}^{-1}$

[B] $5.0 \times 10^{-4} \text{ mm}^{-1}$

[C] $9.0 \times 10^{-4} \text{ mm}^{-1}$

[D] $1.0 \times 10^{-4} \text{ mm}^{-1}$

62. The molecule that is equally well described by single determinantal molecular orbital and simple valence bond theories is



63. The π -electron charges on the four carbon atoms of *trans*-1,3-butadiene are in the ratio

[A] 1:1:1:1

[B] 1:2:2:1

[C] $1:\sqrt{2}:\sqrt{2}:1$

[D] 1:3:3:1

64. The dissociation constant of a weak acid (K_a) can be expressed as [C and λ are the concentration and conductance of the acid, respectively; λ_0 is the conductance of the acid at infinite dilution]

[A] $\frac{\lambda C}{(\lambda_0 - \lambda)}$

[B] $\frac{\lambda^2 C}{\lambda_0(\lambda_0 - \lambda)}$

[C] $\frac{\lambda^2 C}{\lambda_0^2}$

[D] $\frac{\lambda^2 C}{\lambda_0(\lambda - \lambda_0)}$

65. A polymer sample has two types of chains having different molecular weights as shown in the table

	weight fraction	molecular weight
A	0.10	10^4
B	0.90	10^5

The number average molecular weight of the polymer is

[A] 5.26×10^4

[B] 5.26×10^3

[C] 9.1×10^4

[D] 9.1×10^3

66. For a cell reaction, $\text{Hg}_2\text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{Hg} + 2\text{H}^+ + 2\text{Cl}^-$, the standard cell potential at 25°C is 0.25 V and the temperature coefficient of the standard cell potential is $-3.2 \times 10^{-4} \text{ VK}^{-1}$. The standard enthalpy of the reaction (in kJ mol^{-1}) is close to

- [A] -66 [B] -33
[C] 66 [D] 33

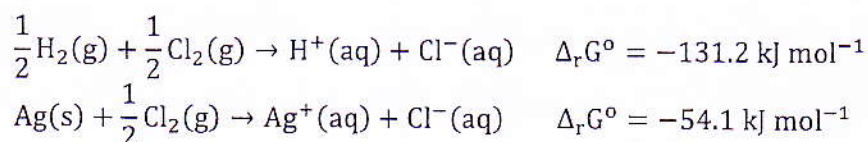
67. The ^1H NMR spectrum of an AB spin system in a 60 MHz spectrometer produces four lines at 423.0 , 418.5 , 416.0 , and 411.5 Hz with reference to TMS. The coupling constant J_{AB} is

- [A] 2.5 Hz [B] 7.0 Hz
[C] 4.5 Hz [D] 11.5 Hz

68. The diffusion coefficient of glycine molecule in water at 25°C is $1.055 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. The time required (in seconds) for a glycine molecule to have a root mean square displacement of 1.0 cm is

- [A] 5.0×10^3 [B] 4.7×10^4
[C] 9.0×10^2 [D] 10

69. Given the following standard molar Gibbs energy of reactions,



the standard molar Gibbs energy of formation of $\text{Ag}^+(\text{aq})$ ions (in kJ mol^{-1}) is

- [A] -77.1 [B] $+77.1$
[C] $+185.3$ [D] -185.3

70. The vapor pressure of a liquid in a particular temperature range follows the equation, $\ln p = 14.9 - \left(\frac{2610.6}{T}\right)$ with pressure, p in Torr and temperature, T in K. Value of the enthalpy of vaporization of the liquid (in kJ mol^{-1}) is

- [A] 21.7 [B] 14.9
[C] 2.6 [D] 0.2

71. The correct relation between the thermodynamic entropy, S and the probability of microstates, p_i is

[A] $S = -k_B \sum_i p_i \ln p_i$

[B] $S = -k_B T \sum_i p_i \ln p_i$

[C] $S = -k_B \sum_i \ln p_i$

[D] $S = - \sum_i p_i \ln p_i$

72. The vibrational wave number of $\text{H}_2(\text{g})$ is 4320 cm^{-1} . This corresponds to a vibrational temperature (in K) of

[A] 777

[B] 1555

[C] 3110

[D] 6220

73. The excited state of a molecule lies at 540 cm^{-1} above the ground state. If both states are nondegenerate, the temperature (in K) at which 10% of the molecules will be in the upper state is

[A] 300

[B] 354

[C] 259

[D] 432

74. The rotational symmetry number for the molecules NH_3 and CH_4 are respectively,

[A] 12, 3

[B] 3, 4

[C] 4, 3

[D] 3, 12

75. The commutator $[\hat{x}^2, \hat{p}_x] =$

[A] $2i\hbar x$

[B] $2i\hbar$

[C] $2i\hbar p_x$

[D] $2i\hbar x p_x$

76. A particle is described by the wave function: $f(x) = \sqrt{a} e^{-ax}$ ($a > 0$).

The length (L) of the interval $-L \leq x \leq L$ in which the particle can be found with 40% probability is

[A] $L = -\frac{1}{2a} \ln(0.6)$

[B] $L = -\frac{1}{2a} \ln(0.4)$

[C] $L = -\frac{1}{2a} \ln(0.5)$

[D] $L = -\frac{1}{2a} \ln(0.3)$

77. The minimum of the following function $V(r)$ is

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

[A] $-\varepsilon$

[B] $-\sigma\varepsilon$

[C] $-\sigma$

[D] σ

78. For a first order reaction, ratio of the time required for 99% completion to that for 90% completion is

[A] 1

[B] 2

[C] 3

[D] 4

79. The modes of *trans*-1,3-butadiene that are Frank-Condon active in a $\pi \rightarrow \pi^*$ excitation, belong to the irreducible representation

[A] A_g

[B] A_u

[C] B_g

[D] B_u

80. An element forms crystals with face-centered cubic (*fcc*) lattice as well as body-centered cubic (*bcc*) lattice. Ratio of the densities of the crystals, ρ_{fcc}/ρ_{bcc} is

[A] 2.000

[B] 1.089

[C] 0.918

[D] 0.544