GS-2024 (Chemistry) X

Full Name :

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Roll No. :

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TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY**

December 10th, 2023

Duration: Three hours (3 hours)

Please read all instructions carefully before you attempt the questions.

1. Write your FULL NAME and ROLL NUMBER (see hall ticket) in block letters, both on this page and on your answer sheet (at the end of this booklet).
2. This is a multiple-choice question paper with **ONE** section having a total of 40 questions. Each correct answer will get you 3 marks. Every wrong answer will get you -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.
3. Indicate your answers on the ANSWER SHEET by filling completely in the appropriate boxes. Do not mark more than one box for any question; this will be treated as an incorrect answer.
4. We advise you to first mark the correct answers in the QUESTION SHEET, and later transfer them to the ANSWER SHEET only when you are sure of your choice.
5. Rough work may be done on the back of the QUESTION SHEET. If needed, you may ask for extra rough sheets from an invigilator.
6. In answering the questions, please choose the option that best describes the solution to the problem.
7. **Use of calculators is permitted in this subject test.**

SOME USEFUL DATA

Avogadro number = 6.02×10^{23} mol^{-1}
RT/F = 0.0257 V at 25°C
Faraday constant = 96500 C/mol
Boltzmann constant $k_B = 1.38\times10^{-23}$ J K^{-1}
Mass of an electron = 9.109×10^{-31} kg

e = 1.6×10^{-19} C
h = 6.626×10^{-34} J s
c = 3×10^{8} m s^{-1}
R = 8.314 J K^{-1} mol^{-1}

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1. A particle in its ground state, given by the wavefunction $\psi_g(x,y,z)$, is excited to a new state $\psi_e(x,y,z)$, if **r** represents the position vector of the particle, the displacement in the particle`s position upon excitation is given by:

   A) $\int \psi_e^* \boldsymbol{r}\, \psi_e dxdydz - \int \psi_g^* \boldsymbol{r}\, \psi_g dxdydz$

   B) $\int \psi_e^* \boldsymbol{r}\, \psi_g dxdydz - \int \psi_g^* \boldsymbol{r}\, \psi_e dxdydz$

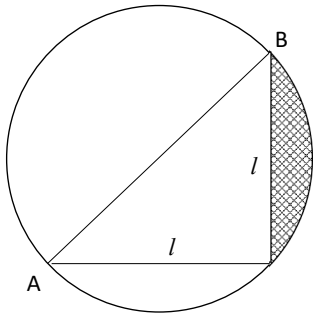
   C) $\int \psi_g^* \boldsymbol{r}\, \psi_e dxdydz$

   D) $\int \psi_e^* \boldsymbol{r}\, \psi_e dxdydz$

2. The volume of a parallelepiped formed by three vectors: $\boldsymbol{A} = 1\boldsymbol{i} + 2\boldsymbol{j}$, $\boldsymbol{B} = 4\boldsymbol{k}$, and $\boldsymbol{C} = 2\boldsymbol{i} + 2\boldsymbol{j}$ is

   A) 8 cubic units
   B) 0 cubic units
   C) 10 cubic units
   D) 12 cubic units

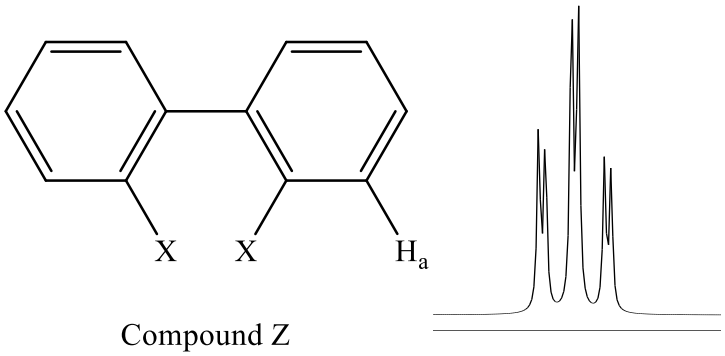
3. Find the shaded area of the circle with radius r, where AB is its diameter.



   A) $(\pi/4 - ½)\ r^2$
   B) $(\pi - 2)\ r^2$

C) $(\pi/4 - 1)\ r^2$
D) $(\pi/4 - 2)\ r^2$

4. In the ^{1}H-NMR of compound Z, if the peak for H_a is as shown, with three coupling constants as 8.0, 7.5, and 1.5, what is the substituent X?



Compound Z

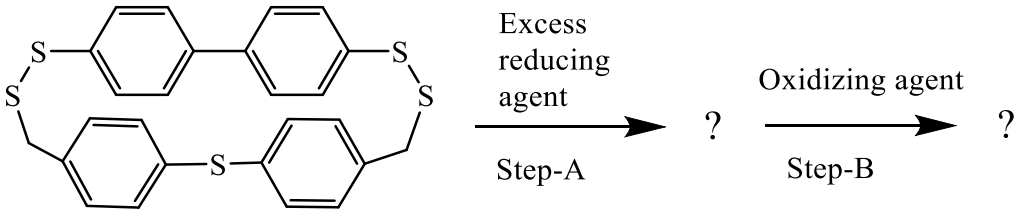
A) F

B) Cl

C) CH_3

D) OCH_3

5. A solution of 1 mM of Compound Z in 1:1 water:methanol, is subjected to the following two reactions. Predict how many products are expected in each step.



Compound Z

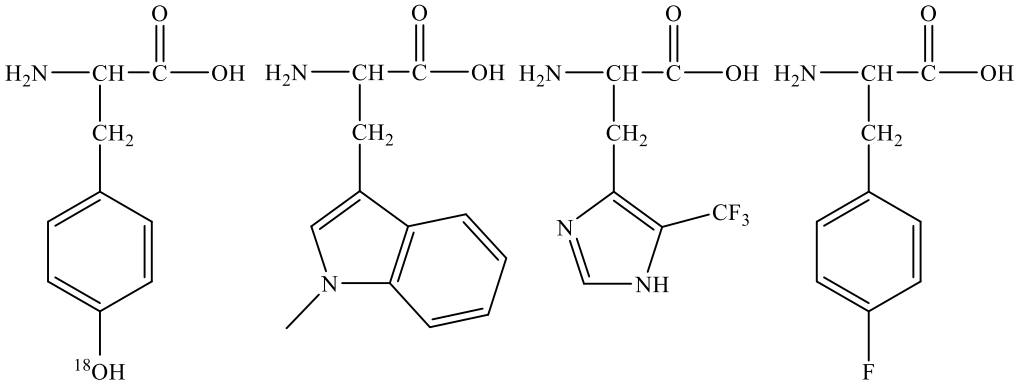
A) Step-A, 3 products; Step-B, 1 product

B) Step-A, 2 products; Step-B, 2 products

C) Step-A, 2 products; Step-B > 10 products

D) Step-A, 3 products; Step-B, 3 products

6. A peptide with an amino acid sequence, KKKRRAAVXPRRRA, had an unknown amino acid X. Identify which of the amino acids shown below could be X if the peptide upon reaction with p-NO_2-$PhN_2^+Cl^-$ provides a product that absorbs at 325 nm.



A) None of the above

B) TIFR-1, TIFR3, and TIFR-4

C) TIFR-1, TIFR-2, and TIFR-4

D) All of the above

7. Consider the following bimolecular reaction: A + B → P, where the rate law is Rate = k[A][B]. Initial concentrations of the reactants are $[A_0] = 1.0 \times 10^{-3}$ M and $[B_0] = 2.0$ M. After 10 seconds, the concentration of A is 1.0×10^{-4} M. Calculate the value of k for the reaction.

A) 2.302 s^{-1}

B) 0.1151 M^{-1} s^{-1}

C) 2.302 M^{-1} s^{-1}

D) 1.151 M^{-1} s^{-1}

8. Which of the following compounds are aromatic?

I **II** **III** **IV**

(A) I, III and IV

(B) I and IV

(C) I, II and IV

(D) I, II, III and IV

9. Consider a system of N non-interacting particles that have two states each, 1 and 2. $E_1 = 0$and $E_2 = \epsilon$. What is the entropy of the system with energy $E = m\epsilon$?

A) $S(m) = k_B log\left(\frac{N!}{m!(N-m)!}\right)$

B) $S(m) = k_B log\left(\frac{N!}{m!}\right)$

C) $S(m) = k_B log\left(\frac{N!}{(N-m)!}\right)$

D) $S(m) = k_B m log(N)$

10. A 1 mm thick transparent crystal of a metalloprotein absorbs 75% of the incident light of wavelength 500 nm. What is the extinction coefficient? (Density of the crystal is 1.5 g/cc, molecular weight of the protein is 100 KDa)

A) 4.00 E-7 $M^{-1}cm^{-1}$

B) 1.66 E+2 $M^{-1}cm^{-1}$

C) 4.00 E+2 $M^{-1}cm^{-1}$

D) 4.0 E+4 $M^{-1}cm^{-1}$

11. NaCl, KCl, NaBr and KBr crystallize in FCC lattices. Their anion and cation touch along the edge of the unit cell. The dimensions of their unit cells are 562.8 pm, 627.7 pm, 596.2 pm, and 658.6 pm, respectively. From these data, what can you say about the size of the ionic radii (within an error of about 5%)?

A) Ionic radii of the cations depend on the nature of the anions.

B) Ionic radii of the anions depend on the nature of the cations.

C) Both (A) and (B).

D) Ionic radii are independent of the counter ions.

12. 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.

13. The lattice energy of solid NaCl is 180 kcal/mole. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal/mole. If the hydration energies of Na^+ and Cl^- ions are in the ratio 6:5, what is the enthalpy of hydration of sodium ion?

A) -85.6 kcal/mole

B) -97.6 kcal/mole

C) 82.6 kcal/mole

D) none of the above

14. The term symbol for a particular atomic state is quoted as $^3S_1$. What is the value of L, S and J for this electronic state?

A) 0,2,1
B) 1,3,1
C) 0,1,1
D) 0,0,1

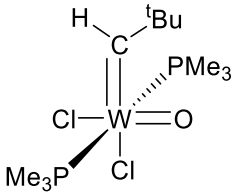
15. Calculate the work done when 50 g of iron reacts with sufficient hydrochloric acid to produce hydrogen gas in (i) a closed insulated vessel (ii) an open beaker at 25^0 C. Molar mass of Fe is 55.85 g mol^{-1}.

A) (i) -1.1 kJ (ii) -2.2 kJ
B) (i) 0.0 kJ (ii) -1.2 kJ
C) (i) 0.0 kJ, (ii) -2.2 kJ
D) (i) -1.1 kJ (ii) 2.2 kJ

16. Calculate the change of entropy ΔS when argon at 25^0 C and 1 atm pressure in a container of volume 500 cm^3 is allowed to expand to 1000 cm^3. Assume isothermal expansion.

A) $\Delta S = 0$ J K^{-1}
B) $\Delta S = 1.110$ J K^{-1}
C) $\Delta S = 1.181$ J K^{-1}
D) $\Delta S = 0.118$ J K^{-1}

17. The oxidation state of tungsten in following complex is



A) +2
B) +4
C) +6
D) +3

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18. Consider the Lyman-α electromagnetic radiation being emitted from a distant star. The light passes through interstellar clouds with an average H atom density of 10^6 atoms / m^3. Assuming the temperature of this cloud to be 3 K, the path length to be 10^{15} meters and the absorption cross-section to be 10^{-17} cm^2/atom, what is the fraction of this radiation absorbed by the interstellar clouds?

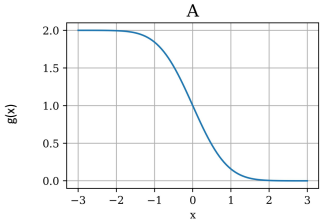
A) 63%
B) 1%
C) 99%
D) 0.1%

19. Consider the following mathematical function:

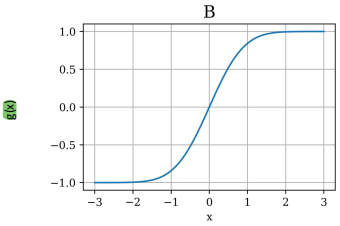
$$g(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

Which of the plots shown below correctly represents this function?

A

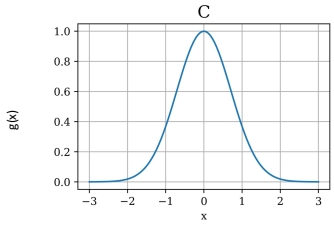


B

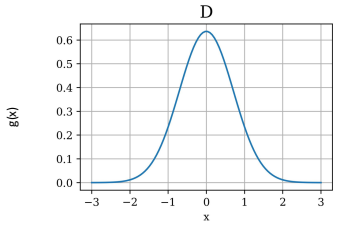


(correct)

C



D



20. Consider an electron microscope in which electrons initially at rest are accelerated through a potential difference of -30 kVolts. Estimate the de Broglie wavelength of the electron after this acceleration.

A) 4×10^{-9} m
B) 1×10^{-13} m
C) 3×10^{-11} m
D) 7×10^{-12} m

21. Consider a proton confined inside a nucleus. Assuming a simplified model such as the proton is confined to a rectangular well with the nucleus of radius 0.5 x 10^{-15} m, calculate the first excitation energy.

A) 0.6 GeV
B) 13.6 eV
C) 0.5 MeV
D) 10.6 GeV

22. Predict the solubility of CaF_2 in a solution of 0.35 M $Ca(NO_3)_2$, CaF_2 solubility product = 4.9 x 10^{-11}

A) 1 x 10^{-11} M
B) 1 x 10^{-6} M
C) 4.9 M
D) 5.9 x 10^{-6} M

23. The state of a spin-1 system is given by $|\psi\rangle = 2|1\rangle + i|0\rangle - i|-1\rangle$, where $|1\rangle$, $|0\rangle$, and $|-1\rangle$ are the eigenstates of the $\widehat{S_z}$ operator. When the z-component of the spin is measured, what is the probability that the system will be found in eigenstate $|-1\rangle$?

A) $-i$

B) $-i/3$

C) $1/3$

D) 1/6

24. The wave function of a particle is given by $\psi(x) = e^{-|x-2|}$. What is the probability that the particle is found in the region $1 < x < 3$?

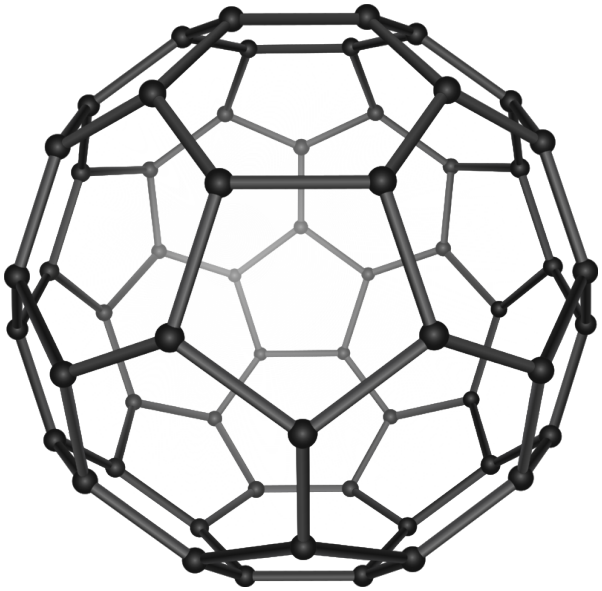
A) -2

B) -0.7689

C) 0.8647

D) 0.7689

25. Identify the symmetry axes present in Buckminster fullerene shown below.



A) C2 and C5

B) C2, C5, C6

C) C2, C3, C5

D) C3, C5, C6

26. What is the primary reason for the reduction in the melting point of nanoparticles as their size decreases?

A) Decreased surface area-to-volume ratio.
B) Strengthened atomic bonds at the surface.
C) Increased proportion of surface atoms.
D) Greater crystal lattice stability.

27. Which quantum mechanical phenomenon is primarily responsible for the tunable emission properties of quantum dots?

A) Quantum entanglement
B) Quantum tunneling
C) Quantum confinement
D) Quantum superposition

28. How long does visible light take to cross 100 μm thick polymer medium with a refractive index of 1.5?

A) 330 fs

B) 500 fs

C) 3.3 fs

D) 0.5 fs

29. In an absorption cell, the transmittance of 0.1 M solution of X is 80%, and that of 0.1 M of Y is 60% at a given wavelength. What is the transmittance of a solution that contains 0.1 M X and 0.1 M Y?

A) 70 %

B) 48 %

C) 37 %

D) 50 %

30. Calculate the number of phases, components, and degrees of freedom present in the system,

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

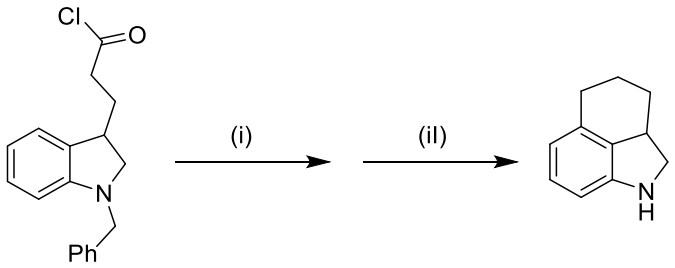
A) P = 3; C = 2; F = 1

B) P = 2; C = 3; F = 3

C) P = 1; C = 2; F = 3

D) P = 2; C = 1; F = 1

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



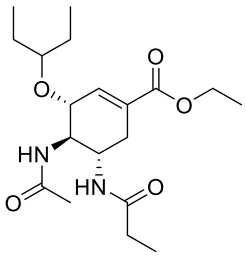
A) (i) NaOH; (ii) Pd/C, H_2 (5 bar)

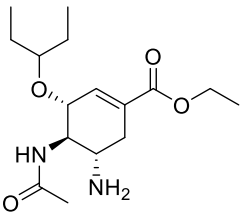
B) (i) Pd/C, H_2 (5 bar); (ii) $AlCl_3$

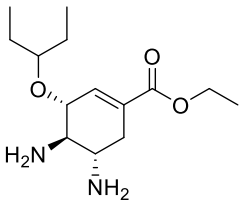
C) (i) $AlCl_3$; (ii) Pd/C, H_2 (5 bar)

D) (i) Pd/C, H_2 (5 bar); (ii) NaOH

32. The octanol-water partition coefficient (Log *P*) for three drugs D1, D2 and D3 are given below. Predict the order of their plasma membrane permeability.







Name	D1	D2	D3
Log *P:*	2.7	1.5	0.5

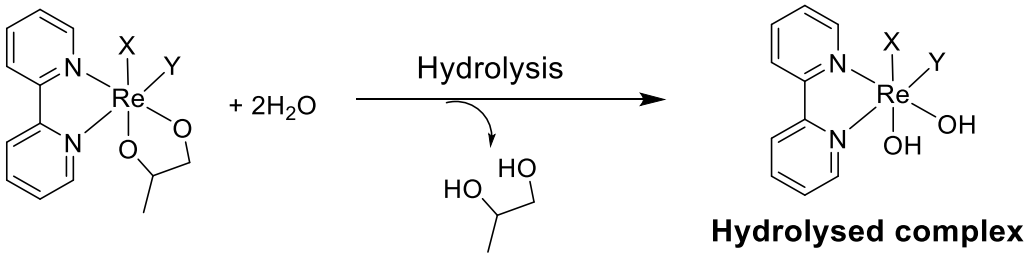
A. D1>D2>D3

B. D3>D2>D1

C. D1=D2>D3

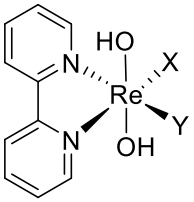
D. D1>D2=D3

33. The hydrolysis of a rhenium complex and the structure of resulting hydrolyzed complex are shown below. The ^{1}H NMR of the hydrolysed complex in D_2O showed a total of four signals (two doublets and two triplets) in the aromatic region corresponding to the bi-pyridine ligand. Predict the correct stereoisomer of the hydrolysed species present in D_2O.

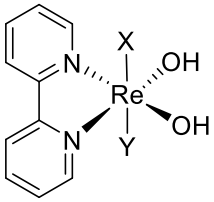


Hydrolysed complex

A.

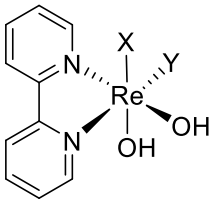


B.

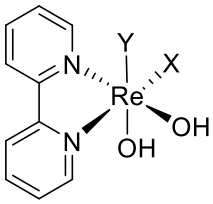


(correct option: B)

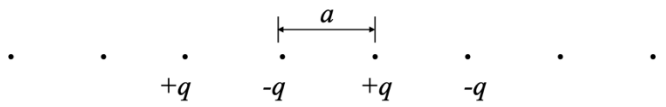
C.



D.



34. For an infinite periodic 1D array of alternating positive and negative charges, separated by a distance, a, what is the net electrostatic-energy per charge (assume that $4\pi\epsilon_0 = 1$):



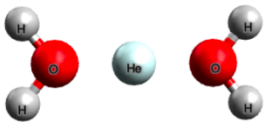
A) $-1.16\frac{q^2}{a}$

B) $\frac{-2q^2}{a}$

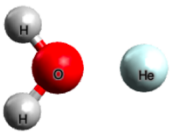
C) $-\frac{2q^2}{a}\ln(2)$

D) $\frac{2q^2}{a}\ln(2)$

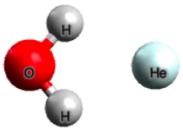
35. The lowest ionization energy of a He atom is 24.4 eV. Its ionization energy can change upon interaction with polar molecules such as water. For the following configurations of He..$(H_2O)_n$ clusters, arrange the He ionization energies, relative to an isolated He atom, in the correct order.



He .. $(H_2O)_2$



He .. $(H_2O)_1$ (I)



He .. $(H_2O)_1$ (II)

A) He > He···$(H_2O)_2$ > He···H_2O (I) > He···H_2O (II)

B) He···H_2O (II) > He > He···H_2O (I) > He···$(H_2O)_2$

C) He···$(H_2O)_2$ > He···H_2O (I) > He···H_2O (II) > He

D) He···$(H_2O)_2$ > He···H_2O (II) > He···H_2O (I) > He

36. Which of the following compounds is diamagnetic?

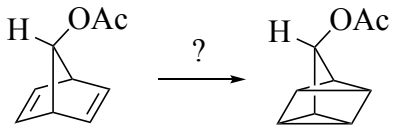
A) $[Mn(CN)_6]^{3-}$

B) $[Co(NH_3)_6]^{3+}$

C) $[Cr(H_2O)_6]^{3+}$

D) $[FeF_6]^{4-}$

37. Predict the reaction condition for the following transformation.



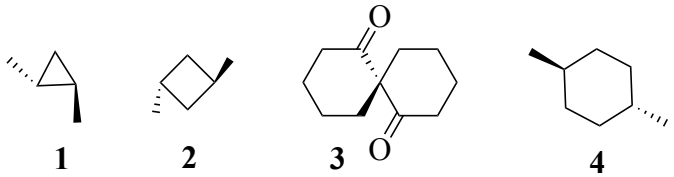
A) heat

B) light

C) acid

D) base

38. Indicate which among the following molecules are achiral.



1 **2** **3** **4**

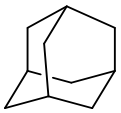
A) 1 & 3

B) 2 & 4

C) 3 & 4

D) 2, 3 & 4

39. How many signals would you expect in ^{13}C NMR of this compound?



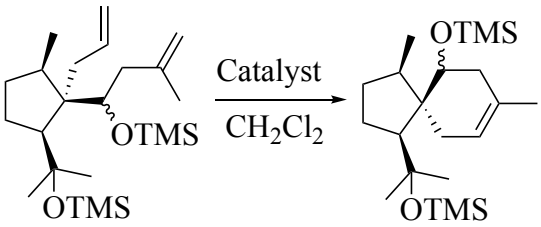
A) 10

B) 8

C) 2

D) 4

40. Which catalyst will lead to the following transformation.



98%

A) $(Cy_3P)_2RuCl_2$=CHPh

B) $RhCl(PPh_3)_3$

C) $PtO_2.H_2O$

D) $Pd(PPh_3)_4$