GATE Chemistry 2022

Question Paper with Detailed Solution

Provided by

ICS Calicut

An Exclusive Center for CSIR-NET & GATE (Chemistry)

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GATE 2022

CY: CHEMISTRY

Duration: Three Hours *Maximum Marks: 100*

GA – GENERAL APTITUDE

Q.1 – Q.5 carry ONE mark each.

1. Inhaling the smoke from a burning __________ could __________ you quickly.

(A) tire / tier (B) tire / tyre
(C) tyre / tire (D) tyre / tier

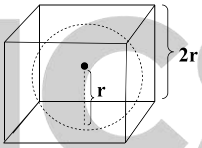
The solution

tyre- rubbery ring
tire- cause to feel in need of rest
[Correct option: C]

2. A sphere of radius r cm is packed in a box of cubical shape. What should be the minimum volume (in cm^3) of the box that can enclose the sphere?

(A) $\frac{r^3}{8}$ (B) r^3
(C) $2r^3$ (D) $8r^3$

The solution



volume of cube = a^3
a = 2r
volume = (2r)^3 = 8r^3
[Correct option: D]

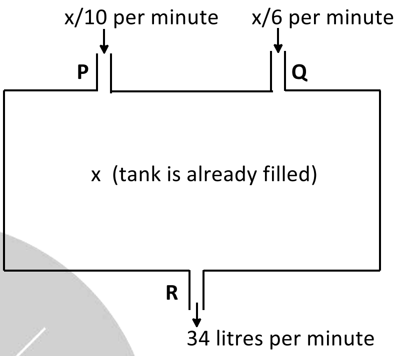
3. Pipes P and Q can fill a storage tank in full with water in 10 and 6 minutes, respectively. Pipe R draws the water out from the storage tank at a rate of 34 litres per minute. P, Q and R operate at a constant rate. If it takes one hour to completely empty a full storage tank with all the pipes operating simultaneously, what is the capacity of the storage tank (in litres)?

(A) 26.8 (B) 60.0
(C) 120.0 (D) 127.5

The solution

Take the capacity of the tank is 'x' liter.
After one hour (60 minutes)

$$\left(\frac{x}{10}\times 60\right)+\left(\frac{x}{6}\times 60\right)+x=34\times 60$$
$$6x+10x+x=2040$$
$$17x=2040$$
$$x=\frac{2040}{17}=120\ litre$$



[Correct option: C]

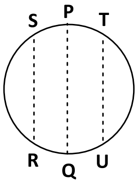
4. Six persons P, Q, R, S, T and U are sitting around a circular table facing the center not necessarily in the same order. Consider the following statements:

- P sits next to S and T.
- Q sits diametrically opposite to P.
- The shortest distance between S and R is equal to the shortest distance between T and U.

Based on the above statements, Q is a neighbour of

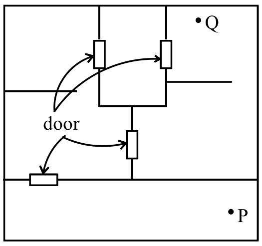
(A) U and S (B) R and T
(C) R and U (D) P and S

The solution



Neighbours of Q are R and U
[Correct option: C]

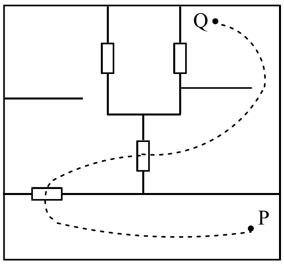
5. A building has several rooms and doors as shown in the top view of the building given below. The doors are closed initially. What is the minimum number of doors that need to be opened in order to go from the point P to the point Q?



(A) 4 (B) 3

(C) 2 (D) 1

The solution



2 doors

[Correct option: C]

Q.6 – Q.10 Carry TWO mark each.

6. Rice, a versatile and inexpensive source of carbohydrate, is a critical component of diet worldwide. Climate change, causing extreme weather, poses a threat to sustained availability of rice. Scientists are working on developing Green Super Rice (GSR), which is resilient under extreme weather conditions yet gives higher yields sustainably.

Which one of the following is the CORRECT logical inference based on the information given in the above passage?

(A) GSR is an alternative to regular rice, but it grows only in an extreme weather

(B) GSR may be used in future in response to adverse effects of climate change

(C) GSR grows in an extreme weather, but the quantity of produce is lesser than regular rice

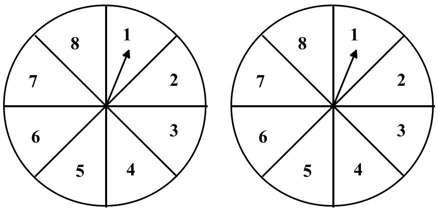
(D) Regular rice will continue to provide good yields even in extreme weather

The solution

Only 2^{nd} option is matches with given information

[Correct option: B]

7. A game consists of spinning an arrow around a stationary disk as shown below. When the arrow comes to rest, there are eight equally likely outcomes. It could come to rest in any one of the sectors numbered 1, 2, 3, 4, 5, 6, 7 or 8 as shown. Two such disks are used in a game where their arrows are independently spun. What is the probability that the sum of the numbers on the resulting sectors upon spinning the two disks is equal to 8 after the arrows come to rest?



(A) $\frac{1}{16}$ (B) $\frac{5}{64}$

(C) $\frac{3}{32}$ (D) $\frac{7}{64}$

The solution

Probability for sum of these 8 are,

(1,7), (7,1), (2,6), (6,2), (3,5), (5,3), (4,4)

Number of chances = 7

Probability for a single number in a disc = 1/8

So, the answer is 7/64

[Correct option: D]

8. Consider the following inequalities.

(i) $3p - q < 4$

(ii) $3q - p < 12$

Which one of the following expressions below satisfies the above two inequalities?

(A) $p + q < 8$

(B) $p + q = 8$

(C) $8 \leq p + q < 16$

(D) $p + q \geq 16$

The solution

Add these equations

$$\begin{array}{r} 3p - q < 4 \\ 3q - p < 12 \\ \hline 2p + 2q < 16 \end{array}$$

dividing by 2; $p + q < 8$

[Correct option: A]

9. Given below are three statements and four conclusions drawn based on the statements.

Statement 1: Some engineers are writers.

Statement 2: No writer is an actor.

Statement 3: All actors are engineers.

Conclusion I: Some writers are engineers.

Conclusion II: All engineers are actors.

Conclusion III: No actor is a writer.

Conclusion IV: Some actors are writers.

Which one of the following options can be logically inferred?

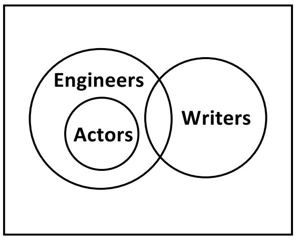
(A) Only conclusion I is correct

(B) Only conclusion II and conclusion III are correct

(C) Only conclusion I and conclusion III are correct

(D) Either conclusion III or conclusion IV is correct

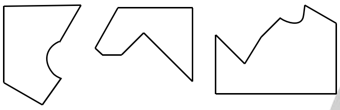
The solution

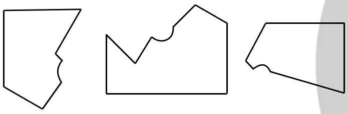


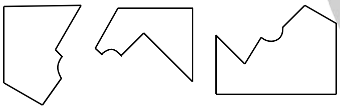
Only I and III are correct

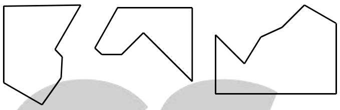
[Correct option: C]

10. Which one of the following sets of pieces can be assembled to form a square with a single round hole near the centre? Pieces cannot overlap.

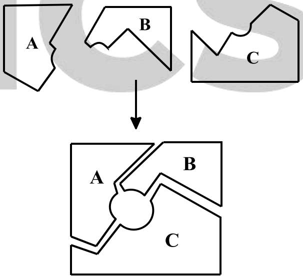
(A)


(B)


(C)


(D)


The solution

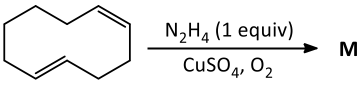


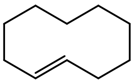
[Correct option: C]

CY – CHEMISTRY

Q.11 – Q.25(MCQ) carry ONE mark each.

11. The major product **M** formed in the following reaction is



(A)


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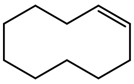
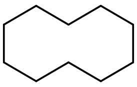
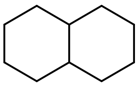


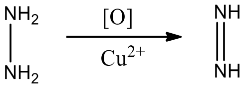
(C)


(D)


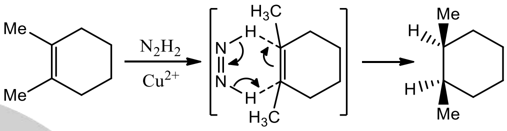
The solution

Reduction of alkenes using diimide

Preparation:

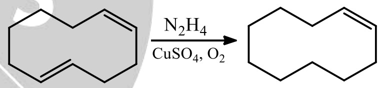


Reaction:



- Syn-addition
- All supra process ($\sigma_s^2 + \sigma_s^2 + \pi_s^2$)
- Trans alkene reacts more rapidly than cis alkene in general.

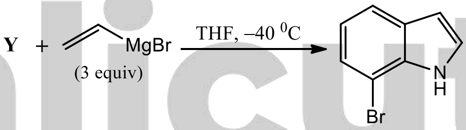
Here

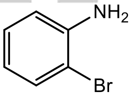


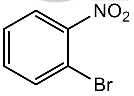
(Reactivity: trans >> cis)

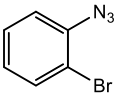
[Correct option: B]

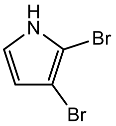
12. The starting material Y in the following reaction is



(A)


(B)


(C)


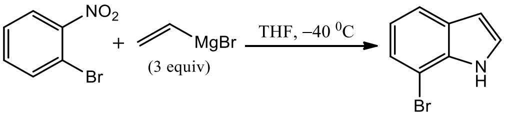
(D)


The solution

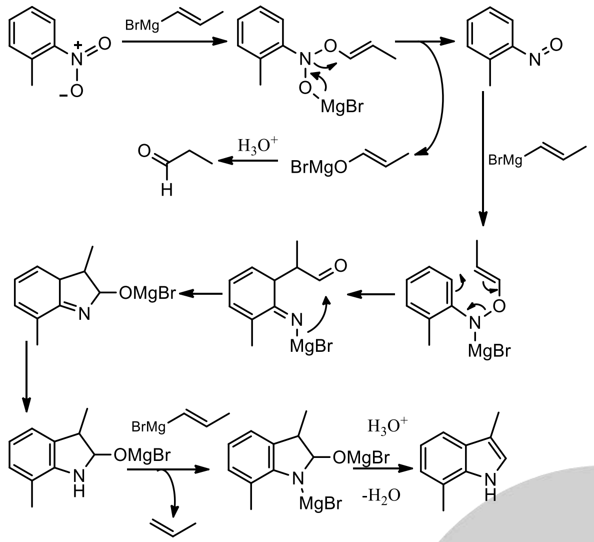
Bartoli Indole synthesis

The chemical reaction of ortho substituted nitro amines (R-NO_2) and nitroso amines ($R - N = O$) with vinyl Grignard reagent to form substituted indole.

Hence

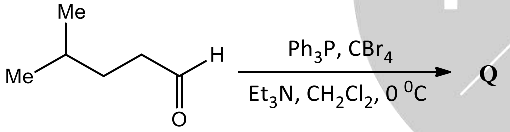


Mechanism:



[Correct option: B]

13. The major product in the given reaction is **Q**. The mass spectrum of **Q** shows{[M] = molecular ion peak}



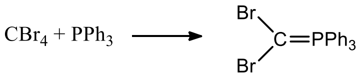
(A) [M], [M+2] and [M+4] with relative intensity of 1:2:1

(B) [M] and [M+2] with relative intensity of 1:1

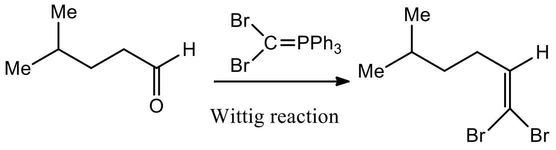
(C) [M], [M+2] and [M+4] with relative intensity of 1:3:1

(D) [M] and [M+2] with relative intensity of 2:1

The solution



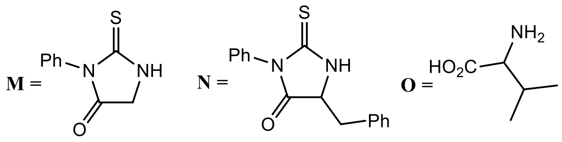
Corey- Fuchs reaction



two bromine atoms are present, so 1:2:1

[Correct option: A]

14. A tripeptide on treatment with PhNCS (pH = 8.0) followed by heating with dilute HCl afforded a cyclic compound **M** and a dipeptide. The dipeptide on treatment with PhNCS (pH = 8.0) followed by heating with dilute HCl afforded a cyclic compound **N** and an acyclic compound **O**. The CORRECT sequence (from N- to C-terminus) of the tripeptide is



(A) glycine-phenylalanine-valine

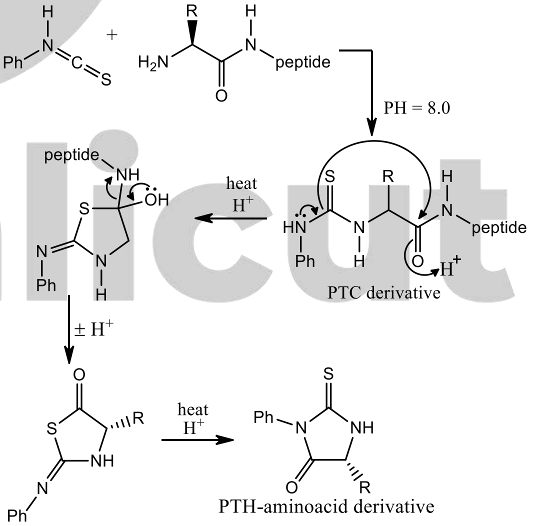
(B) valine-phenylalanine-glycine

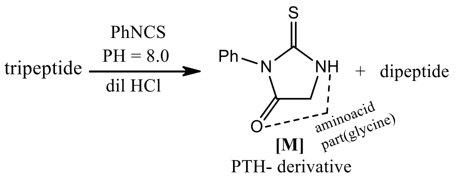
(C) glycine-tyrosine-valine

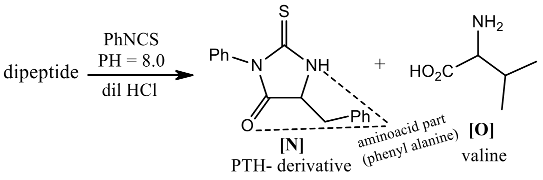
(D) glycine-phenylalanine-alanine

The solution

This is Edman degradation. In this method phenylisothiocyanate(PITC) is reacted with an uncharged N-terminal amino group under mild alkaline condition to form phenylthio carbonyl derivative (PTC derivative). Then under acidic condition this derivative of terminal amino acid is cleaved as thiazolinone derivative (ATZ derivative). The thiazolinone amino acid is then selectively extracted into an organic solvent and treated with acid to form more stable phenylthiohydantoin (PTH amino acid derivative). PTH amino acid derivative can be identified using chromatography. The procedure can then be repeated again to identify the next amino acid.





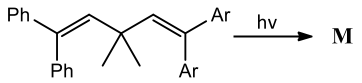


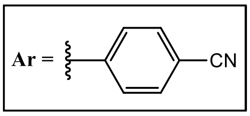
Sequence will be,

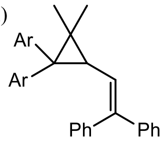
Glycine – Phenylalanine – Valine

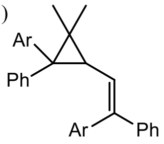
[Correct option: A]

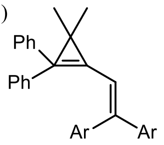
15. The major product **M** in the following reaction is

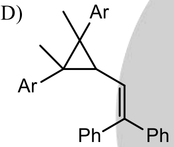




(A)


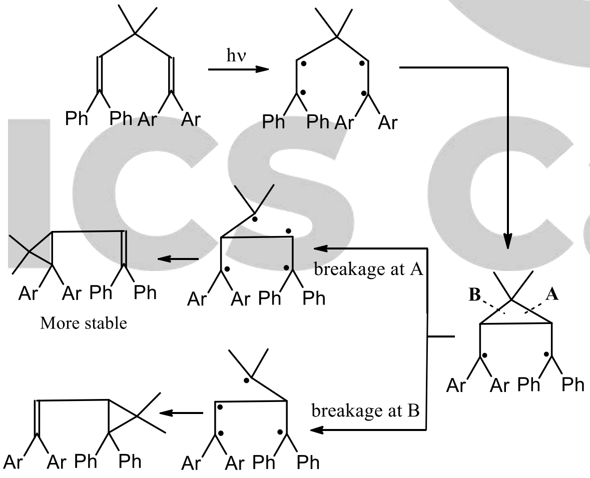
(B)


(C)


(D)


The solution

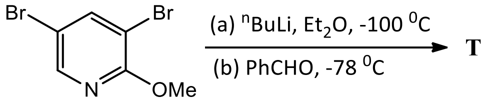
It is an example for di pi methane rearrangement.

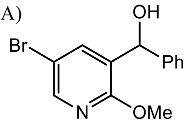


Generally, the product with electron donating group with unsaturation (double bond) and electron withdrawing group with ring is more stable.

[Correct option: A]

16. The major product **T** formed in the following reaction is



(A)


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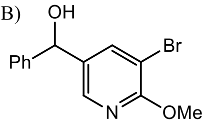
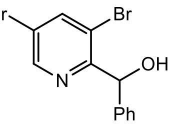
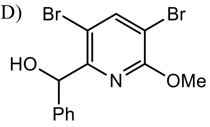
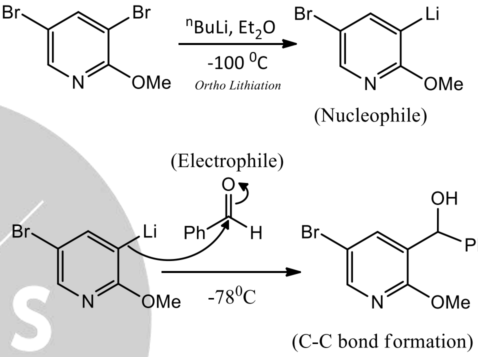


(C)


(D)


The solution



[Correct option: A]

17. In differential thermal analysis (DTA)

(A) the temperature differences between the sample and reference are measured as a function of temperature

(B) the differences in heat flow into the reference and sample are measured as a function of temperature

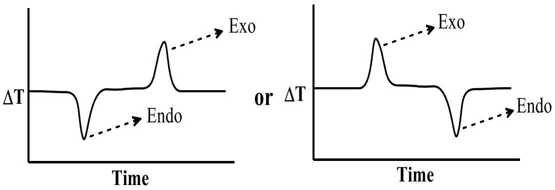
(C) the change in the mass of the sample is measured as a function of temperature

(D) the glass transition is observed as a sharp peak

The solution

DTA technique measure the difference in temperature between the sample and a reference material (DT).

ie, Temperature change against time.



[Correct option: A]

18. The ν_{0-0}resonance Raman stretching frequency (cm^{-1}) of the coordinated dioxygen in oxy-hemoglobin and oxy-hemocyanin appears, respectively, nearly at

(A) 1136 and 744 (B) 1550 and 744
(C) 744 and 1136 (D) 744 and 1550

The solution

Metalloprotein	Species coordinate d to metal centre(s)	ν_{0-0}resonance Raman stretching frequency (cm^{-1})
oxy-hemoglobin	O_2^-	1105 cm^{-1} (~1136 cm^{-1})
oxy-hemocyanin	$\eta^2;\eta^2 O_2^-$	803 cm^{-1} (744 cm^{-1})

[Correct option: A]

19. The number of metal-metal bond(s), with σ, π, and δ character, present in [$Mo_2(CH_3CO_2)_4$] complex is(are), respectively,

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

The solution

[$Mo_2(CH_3CO_2)_4$] is a complex with quadrupole bonds.

2x – 4 = 0

2x = 0

x = 4/2 = +2

i.e Mo^{2+}

- Mo^{2+} is d^4 system
- 8 electrons from two Mo atoms
- Electronic configuration

$$\sigma^2 < \pi^4 < \delta^2 < \delta^{*0}$$

i.e Mo≣Mo type

1- σ type

2- π type

1- δ type

[Correct option: A]

20. 1s_A and 1s_B are the normalized eigenfunctions of two hydrogen atoms H$_A$ and H$_B$, respectively. If $S = \langle 1s_A | 1s_B \rangle$, the option that is ALWAYS CORRECT is

(A) S = 1
(B) S = 0
(C) S = imaginary constant
(D) 0 ≤ S ≤ 1

The solution

The extent to which two atomic orbitals overlap is measured by the overlap integral 'S'.

$$S = \langle 1s_A | 1s_B \rangle = \int \psi_A^* \psi_B d\tau$$

- If two normalized atomic orbitals are identical then S = 1
- If the integral over the region where the product of the wave function is positive exactly cancels the integral over the region where the product is negative, so overall S = 0 (as in case of 'S' and 'P$_x$' orbital)

ie. 0 ≤ S ≤ 1

[Correct option: D]

21. The pure vibrational spectrum of a hypothetical diatomic molecule shows three peaks with the following intensity at three different temperatures.

Peak	Intensity (arbitrary unit)		
	300 K	600 K	900 K
I	1.0	1.0	1.0
II	0.1	0.1	0.1
III	0.02	0.04	0.06

The CORRECT statement is

(A) Peak I appears at the lowest energy
(B) Peak II appears at the lowest energy
(C) Peak III appears at the lowest energy
(D) Peak I appears at the highest energy

The solution

For an anharmonic oscillator

< i > fundamental bond will observe

at, $\Delta E_{0\to1} = \omega_e - 2\,\omega_e x_e$

<ii> first hot band, $\Delta E_{1\to2} = \omega_e - 4\,\omega_e x_e$

<iii> first overtone, $\Delta E_{0\to2} = 2\omega_e - 6\,\omega_e x_e$

Here $\omega_e = \hbar\omega = h\nu$

By taking an arbitrary value for ω_e = 1000 and x_e = 0.01 we get

$\Delta E_{0\to1}$ = 1000 – (2 x 1000 x 10^{-2}) = 980

$\Delta E_{1\to2}$ = 1000 – (4 x 1000 x 10^{-2}) = 960

$\Delta E_{0\to2}$ = 2000 – (6 x 1000 x 10^{-2}) = 1940

The order of energy is

$\Delta E_{1\to2} < \Delta E_{0\to1} < \Delta E_{0\to2}$

Peak one must be fundamental band ($\Delta E_{0\to1}$). since it have highest intensity

Peak III may be first hot band ($\Delta E_{1\to2}$). since its intensity increasing with increase in temperature.

Peak IInd probably first overtone since it has low value of intensity compare to 1st.

By this we can conclude that the correct statement is,

Peak III (first hot band $\Delta E_{1\to2}$) appear at lowest energy.

[Correct option: C]

22. The point group of SF$_6$ is

(A) D$_{6h}$ (B) O$_h$
(C) D$_{6d}$ (D) C$_{6v}$

The solution

The point group of SF$_6$ is O$_h$

O$_h$	E	8C$_3$	6C$_2$	6C$_4$	3C$_2$	i	6S$_4$	8S$_6$	3σ_h	6σ_d

Number of classes = 10

Number of elements = 48

[Correct option: B]

23. A point originally at (1, 3, 5) was subjected to a symmetry operation ($\hat{O}_1$) thatshifted the point to (−1, −3, 5). Subsequently, the point at (−1, −3, 5) was subjected to another symmetry operation ($\hat{O}_2$) that shifted this point to (−1, −3, −5). The symmetry operators $\hat{O}_1$and $\hat{O}_2$are, respectively,

(A) $\hat{C}_2(x)$ and $\hat{\sigma}(xy)$

(B) $\hat{C}_2(z)$ and $\hat{\sigma}(xy)$

(C) $\hat{\sigma}(xy)$ and $\hat{C}_2(z)$

(D) $\hat{S}_1$ and $\hat{S}_2$

The solution

$$C_2^x(x,y,z) \longrightarrow (x,-y,-z)$$
$$C_2^y(x,y,z) \longrightarrow (-x,y,-z)$$
$$C_2^z(x,y,z) \longrightarrow (-x,-y,z)$$
and
$$\sigma_{xy}(x,y,z) \longrightarrow (x,y,-z)$$
$$\sigma_{xz}(x,y,z) \longrightarrow (x,-y,z)$$
$$\sigma_{yz}(x,y,z) \longrightarrow (-x,y,z)$$

Here

C_2^z (1, 3, 5) ⟶ (−1, −3, 5)

σ_{xy} (-1, -3, 5) ⟶ (−1, −3, −5)

[Correct option: B]

24. Adsorption of a gas with pressure P on a solid obeys the Langmuir adsorption isotherm. For a fixed fractional coverage, the correct relation between K and P at a fixed temperature is

[$K = k_a / k_b$, k_a and k_b are the rate constants for adsorption and desorption, respectively. Assume non-dissociative adsorption.]

(A) $K \propto P^{-1/2}$ (B) $K \propto P$

(C) $K \propto P^{-1}$ (D) $K \propto P^{1/2}$

The solution

From Langmuir isotherm,

$\theta = \frac{K.p}{1+K.P}$; $K = \frac{k_a}{k_b}$

θ =fractional coverage

$\theta = \frac{V}{V_\infty}$

$\frac{1}{\theta} = \frac{1+K.P}{K.p}$; $\theta = \frac{V}{V_\infty}$

$\frac{1}{\theta} = \frac{1}{K.p} + 1$

$K = \frac{1}{\left(\frac{1}{\theta}-1\right)p}$

For a fixed fractional coverage

K = a constant x 1/p

$K \propto \frac{1}{P}$

i.e $K \propto P^{-1}$

[Correct option: C]

25. The temperature dependence of the rate constant for a second-order chemical reaction obeys the Arrhenius equation. The SI unit of the 'pre-exponential factor' is

(A) s^{-1} (B) $m^3\ mol^{-1}\ s^{-1}$

(C) $mol\ m^{-3}\ s^{-1}$ (D) $(m^3\ mol^{-1})^2\ s^{-1}$

The solution

Arrhenius equation says.

$k = Ae^{-Ea/RT}$

k = rate constant

A = pre exponential factor

E_a = energy of activation (in J mol^{-1})

R= 8.314 J K^{-1} mol^{-1}

T = temperature in Kelvin

The term $\frac{E_a}{RT}$ is dimensionless

$k = Ae^{-Ea/RT}$

unit of pre-exponential factor(A) = unit of rate constant(k)

(since $e^{-Ea/RT}$ have no unit)

Unit of second order rate constant =

$[\text{concentration}]^{-1}[second]^{-1}$

Concentration = mol m^{-3}

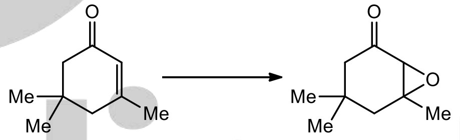
$[\text{concentration}]^{-1}$= m^3mol^{-1}

Unit of k = unit of A = m^3 mol^{-1} s^{-1}

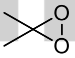
[Correct option: B]

Q.26–Q.32 (MSQ) Carry ONE mark each.

26. The CORRECT reagent(s) for the given reaction is(are)



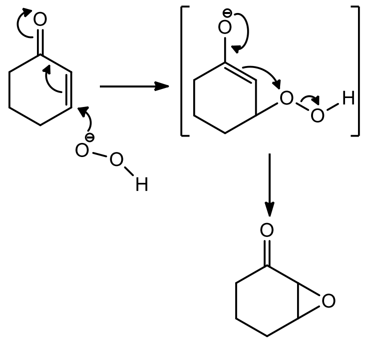
(A) H_2O_2, NaOH

(B) 

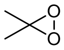
(C) DIBAL-H, then *m*CPBA

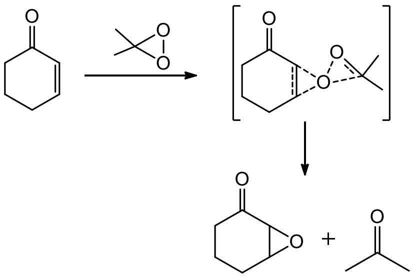
(D) SO_3, pyridine, Me_2SO

The solution



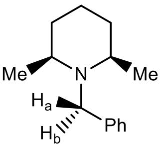
H_2O_2/OH^- is the best oxidizing agent for oxidation of α, β unsaturated carbonyl compounds.

Similarly, the dimethyldioxirane(DMD),  is also used as oxidizing agent.

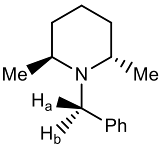


[Correct options: A & B]

27. The CORRECT statement(s) about the ^1H NMR spectra of compounds **P** and **Q** is (are)



P



Q

(A) **P** shows a sharp singlet at δ = 3.70 ppm (for H_a and H_b)

(B) **Q** shows a sharp singlet at δ = 3.70 ppm (for H_a and H_b)

(C) **P** shows a AB-quartet centered at δ = 3.63 ppm (for H_a and H_b)

(D) **Q** shows a AB-quartet centered at δ = 3.63 ppm (for H_a and H_b)

The solution

H_a and H_b in P is enantiotopic and Q is diastereotopic. Enantiotopic atoms or groups give same signal in NMR spectroscopy but diastereotopic atoms or groups give different signals.

[Correct options: A & D]

28. The CORRECT statement(s) about thallium halides is(are)

(A) TlF is highly soluble in water whereas other Tl-halides are sparingly soluble

(B) TlF adopts a distorted NaCl structure

(C) TlI_3 is isomorphic with CsI_3 and the oxidation state of Tl is +3

(D) Both TlBr and TlCl have CsCl structure

The solution

TlF: TlF is a white crystalline solid, which is highly soluble in water unlike the other Tl(I) halides. At normal room temperature it possesses a similar structure to α-PbO which has a distorted rock salt structure. At 62^0C it transforms to a tetragonal structure.

TlCl and TlBr: They have crystal structure same as CsCl.

TlI_3 and CsI_3: TlI_3 is isomorphic with CsI_3, but oxidation number of Tl = +1.

TlI_3 is $Tl^+I_3^-$ and CsI_3 is $Cs^+I_3^-$

[Correct options: A, B & D]

29. The CORRECT statement(s) about the spectral line broadening in atomic spectra is(are)

(A) The collision between atoms causes broadening of the spectral line

(B) Shorter the lifetime of the excited state, the broader is the line width

(C) Doppler broadening is more pronounced as the flame temperature increases

(D) In flame and plasma, the natural line broadening exceeds the collisional line broadening

The solution

Several factors contribute to width of spectral line (broadening of spectra)

i) Natural broadening:- it is a result of Heisenberg's uncertainty principle which indicates that there is an uncertainty in the energy state of the system.

$\Delta E.\Delta t = \frac{h}{2\pi}$, here ΔE, Δt represents uncertainties of energy and time.

$\Delta E = \frac{h}{2\pi.\Delta t}$

Decreasing lifetime increase the energy uncertainty and spectral line will become broader.

ii) Collision broadening:- atoms and molecules in ligand and gaseous phases are in continual motion and collide frequently with each other, these collision perturb the energy levels and cause broadening.

iii) Doppler broadening:- in liquids and gases (or plasma) the motion is random in a given sample, shift to both high and low frequencies occur and hence the spectral line is broadened.

Increase in temperature increases the kinetic energy (velocity) of molecule and cause more broadening.

NB:- refer Doppler effect

Option A, B and C are correct

In flame and plasma collisional line broadening exceeds natural line broadening hence option four is incorrect.

[Correct options: A, B & C]

30. Match the CORRECT option(s) from column A with column B according to the metal centre present in the active site of metalloenzyme.

A		B	
P	Cu	**I**	B_{12}-coenzyme
Q	Mo	**II**	Carboxypeptidase
R	Co	**III**	Nitrate reductase
S	Zn	**IV**	Cytochrome P-450
		V	Tyrosinase

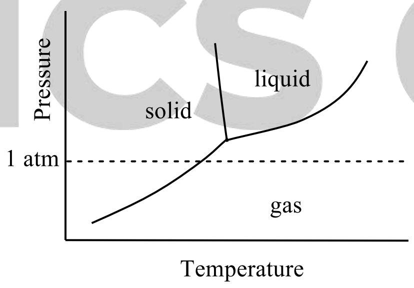
(A) P-V, Q-III, R-I, S-II
(B) P-IV, Q-II, R-I, S-III
(C) P-II, Q-IV, R-V, S-III
(D) P-V, Q-III, R-II, S-IV

The solution

	Metallo-protein	Metal centre present in active site	functions
1.	B_{12}	Co	Group transfer reaction
2.	Carboxy peptidase	Zn	Hydrolysis of peptide bond
3.	Nitrate reductase	Mo	Reduction of nitrate to nitrite
4.	Cytochrome P-450	Fe	Oxidation of alkene
5.	Tyrosinase	Cu	Melanin production

[Correct option: A]

31. The CORRECT statement(s) about the following phase diagram for a hypothetical pure substance **X** is(are)



(A) The molar volume of solid **X** is less than the molar volume of liquid **X**
(B) **X** does not have a normal boiling point
(C) The melting point of **X** decreases with increase in pressure
(D) On increasing the pressure of the gas isothermally, it is impossible to reach solid phase before reaching liquid phase

The solution

I. If molar volume of solid is less than that of liquid. Then the solid- liquid boundary (fusion curve) must have a positive slope in its pressure- temperature graph (phase diagram). Hence first option is incorrect.

II. The normal boiling point (also called the atmospheric boiling point or the atmospheric pressure boiling point) is the case in which the vapor pressure of a liquid equals the defined atmospheric pressure at sea level, one atmosphere. A substance having triple point pressure higher than 1 atm do not show normal boiling point. i.e second option is correct.

III. If $V_m(l) < V_m(S)$, increase in pressure increases the chemical potential of the solid more than that of liquid and this case the freezing temperature is lowered slightly, i.e 3rd option is also correct.

IV. From phase diagram it is clear that by increasing pressure of a gas isothermally we can reach solid state (sublimation) before liquid state.
i.e option four is incorrect.
[Correct options: B & C]

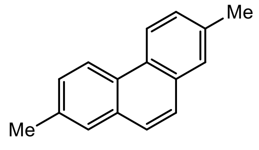
32. The parameter(s) fixed for each system in a canonical ensemble is(are)
(A) temperature (B) pressure
(C) volume (D) composition

The solution

The canonical ensemble is a collection of imaginary replications of the actual system with a common temperature and number of particles. Fixed parameters for a canonical ensemble are temperature (T), volume (V) and number of molecules (N) or composition.
[Correct options: A, C & D]

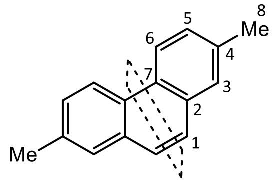
Q.33–Q.35 (NAT) Carry ONE mark each.

33. The number of peaks exhibited by **T** in its broadband proton decoupled ^{13}C NMR spectrum recorded at 25 ^0C in $CDCl_3$ is



T

The solution



8 different type of carbon atom
[Correct answer: 8 to 8]

34. The diffraction angle (in degree, rounded off to one decimal place) of (321) sets of plane of a metal with atomic radius 0.125 nm, and adopting BCC structure is
(Given: the order of reflection is 1 and the wavelength of X-ray is 0.0771 nm)

The solution

Given n = 1, λ = 0.771 nm, r = 0.125 nm and (h k l) = (3 2 1)

According to Braggs law n λ = 2dsinθ

Sinθ = $\frac{n\lambda}{2d}$

d = $\frac{a}{\sqrt{h^2+k^2+l^2}}$

for BCC cube, 4r = $\sqrt{3}$a

a = $\frac{4r}{\sqrt{3}}$

d = $\frac{4r}{\sqrt{3} \text{ x } \sqrt{h^2+k^2+l^2}}$

$= \frac{4 \text{ x } 0.125}{\sqrt{3} \text{ x } \sqrt{3^2+2^2+1^2}} = \frac{4 \text{ x } 0.125}{\sqrt{3} \text{ x } \sqrt{14}}$

Sinθ = $\frac{1 \text{ x } 0.0771 \text{ x } \sqrt{3} \text{ x } \sqrt{14}}{2 \text{ x } 4 \text{ x } 0.125}$

= 0.53

θ = 30

[Correct answer: **30.0 to 31.0**]

35. For the angular momentum operator $\hat{L}$ and the spherical harmonics $Y_{lm}(\theta,\phi)$,

$(\hat{L}_x^2 + \hat{L}_y^2)Y_{21}(\theta,\phi) = n\,\hbar^2 Y_{21}(\theta,\phi)$

The value of nis……

The solution

$l_x = L_x,\ l_y = L_y,\ l_z = L_z$

$L^2 = l_x^2 + l_y^2 + l_z^2$

$l_x^2 + l_y^2 = L^2 - l_z^2$

$L^2 = l(l+1)\hbar^2$

$l_z = \sqrt{m_l}\,\hbar, \quad l_z^2 = m_l\hbar^2$

$l_x^2 + l_y^2 = l(l+1)\hbar^2 - m_l\hbar^2$

$= 2(2+1) - 1 \times \hbar^2 = 5\hbar^2$

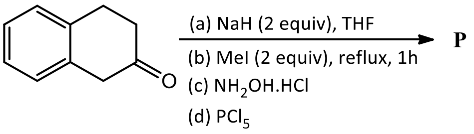
$(\hat{L}_x^2 + \hat{L}_y^2)Y_{21}(\theta,\phi) = 5\hbar^2 Y_{21}(\theta,\phi)$

Therefore, n = 5

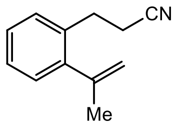
[Correct answer: **5 to 5**]

Q.36 – Q.50 (MCQ) Carry TWO mark each.

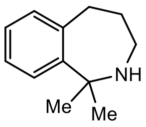
36. The major product **P** obtained in the following reaction sequence is



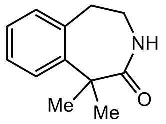
(A)



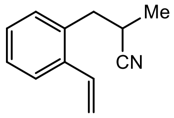
(B)



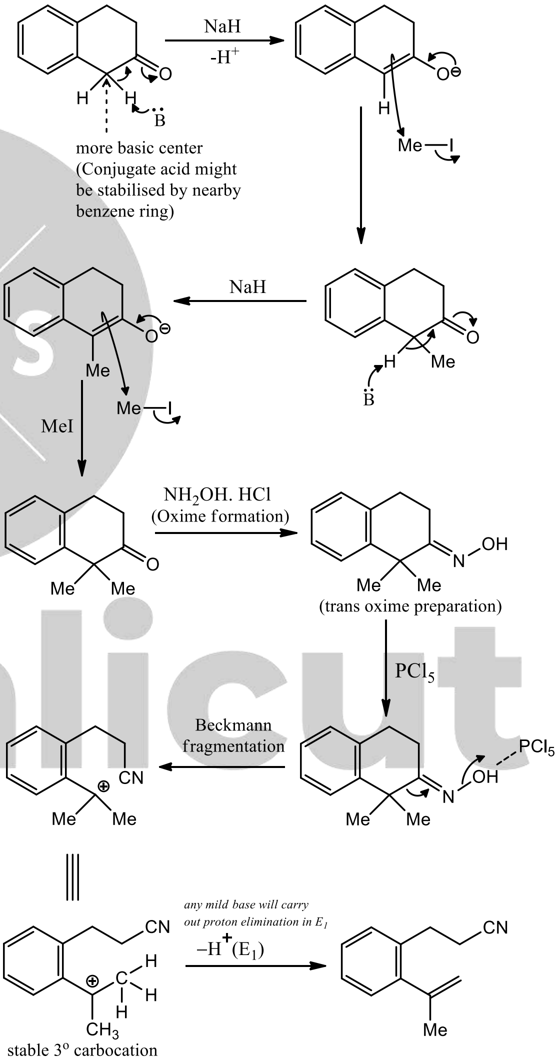
(C)



(D)

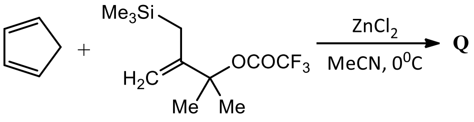


The solution

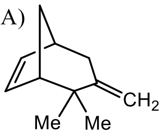


[Correct option: A]

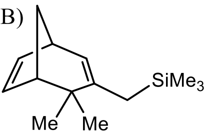
37. The major product **Q** in the given reaction is



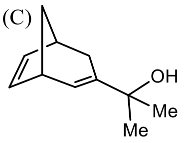
(A)



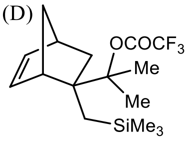
(B)



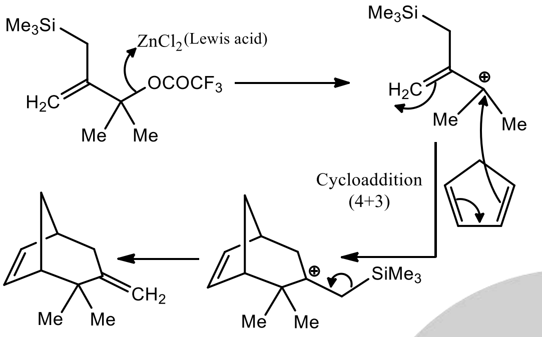
(C)



(D)

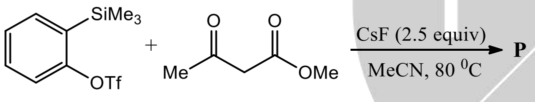


The solution

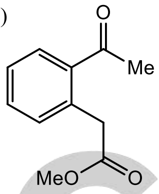


[Correct option: A]

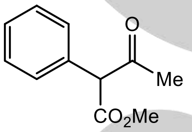
38. The major product P in the following reaction is



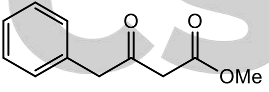
(A)



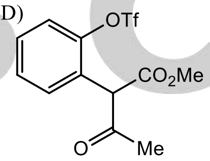
(B)



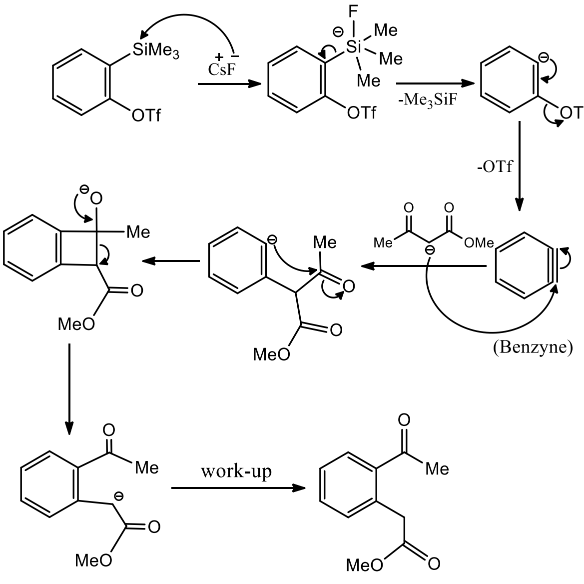
(C)



(D)

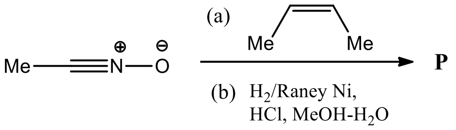


The solution

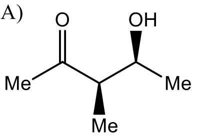


[Correct option: A]

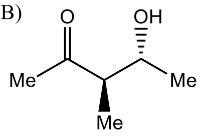
39. The major product **P** in the reaction sequence is



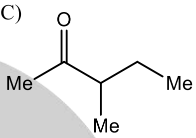
(A)



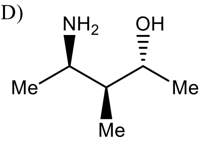
(B)



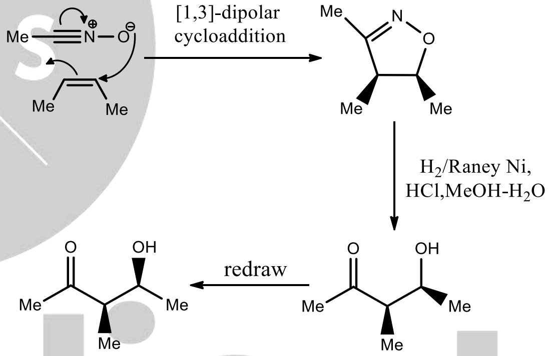
(C)



(D)

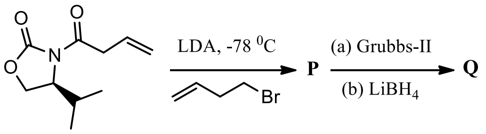


The solution

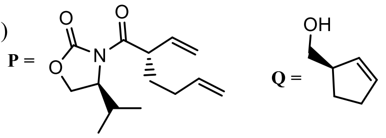


[Correct option: A]

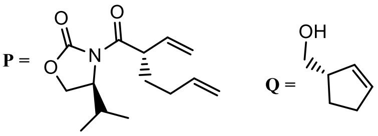
40. The major products **P** and **Q** in the following reaction sequence are



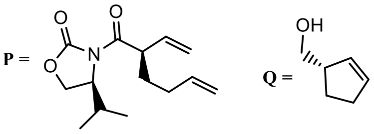
(A)



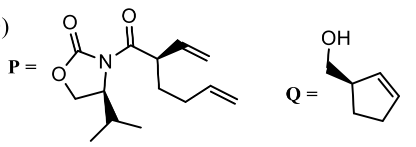
(B)



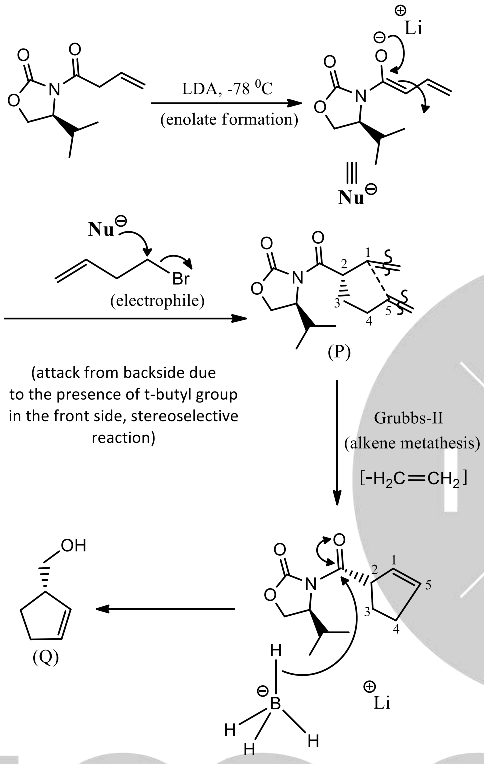
(C)



(D)

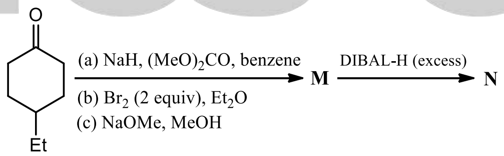


The solution

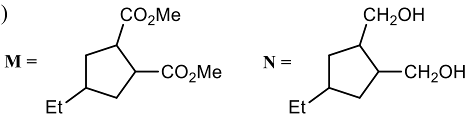


[Correct option: B]

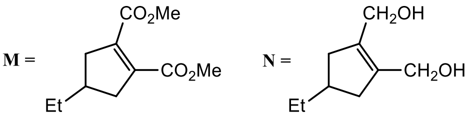
41. The major products **M** and **N** in the given reaction sequence are



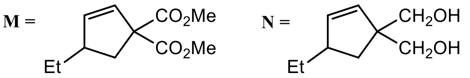
(A)



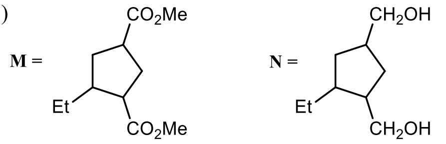
(B)



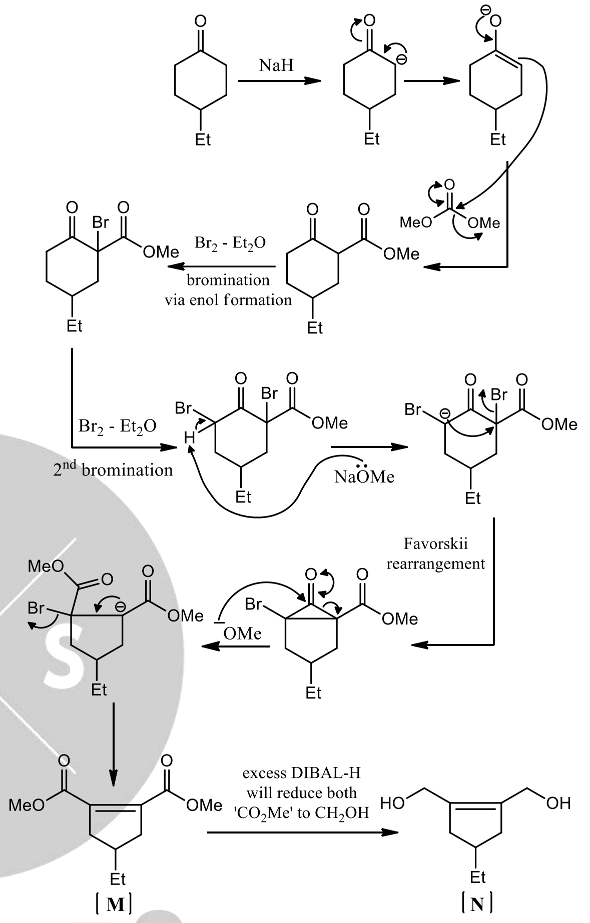
(C)



(D)

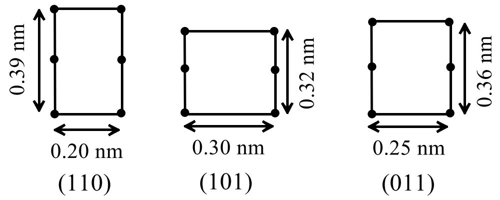


The solution



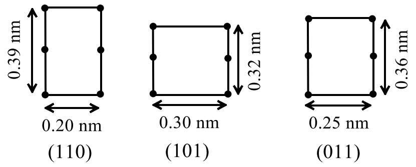
[Correct option: B]

42. Three different crystallographic planes of a unit cell of a metal are given below(solid circles represent atom). The crystal system of the unit cell is



(A) triclinic (B) monoclinic
(C) tetragonal (D) orthorhombic

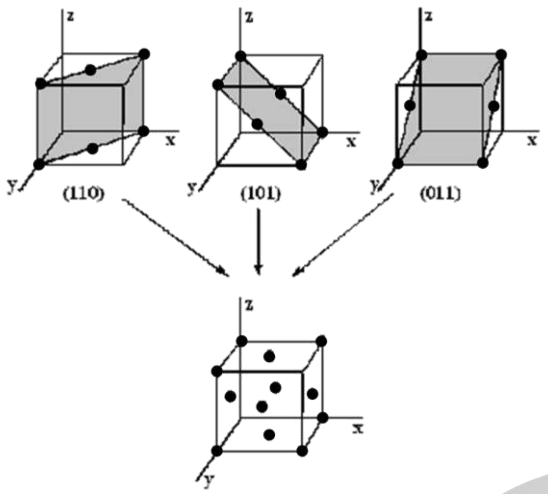
The solution



a=0.20 nm; b=0.30 nm; c=0.25 nm

therefore, $a \neq b \neq c$,

From the given planes,



(all solid circles are in faces)

In case of orthorhombic $a \neq b \neq c$, and possible lattice types are P, B, F, E (from the given planes) or all edge lengths of above unit cell is like a matchbox,

[Correct option: D]

43. The number of equivalents of H_2S gas released from the active site of *rubredoxin,2-iron ferredoxin*, and *4-iron ferredoxin* when treated with mineral acid, respectively, are

(A) 4, 6, 8 (B) 0, 2, 4

(C) 1, 2, 4 (D) 0, 2, 3

The solution

Rubredoxin--- $FeS_0 \longrightarrow 0$

2-iron ferredoxin--- $Fe_2S_2 \longrightarrow 2$

4-iron ferredoxin--- $Fe_4S_4 \longrightarrow 4$

[Correct option: B]

44. The number of $\nu_{S=0}$ stretching vibration band(s) observed in the IR spectrum of the high-spin $[Mn(dmso)_6]^{3+}$ complex (dmso: dimethylsulfoxide) is

(A) only one

(B) two with intensity ratio 1:2

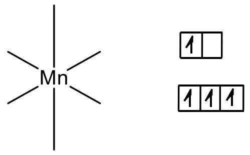
(C) two with intensity ratio 1:1

(D) six with intensity ratio 1:1:1:1:1:1

The solution

High spin $[Mn(dmso)_6]^{3+}$,

- Mn^{3+}, high spin - d^4 system
- Jahn Teller distortion



ie, 2 : 4 = 1 : 2

[Correct option: B]

45.

$$[Fe(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+} \xrightarrow{k_{11}} [Fe(H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+}$$

$$[Fe(bpy)_3]^{2+} + [Fe^*(bpy)_3]^{3+} \xrightarrow{k_{22}} [Fe(bpy)_3]^{3+} + [Fe^*(bpy)_3]^{2+}$$

(bpy = bipyridyl)

$$[Co(NH_3)_6]^{2+} + [Co^*(NH_3)_6]^{3+} \xrightarrow{k_{33}} [Co(NH_3)_6]^{3+} + [Co^*(NH_3)_6]^{2+}$$

*indicates a radioactive isotope

The rate constants in the given self-exchange electron transfer reactions at a certain temperature follow

(A) $k_{11} > k_{22} > k_{33}$ (B) $k_{22} > k_{11} > k_{33}$

(C) $k_{33} > k_{22} > k_{11}$ (D) $k_{22} > k_{33} > k_{11}$

The solution

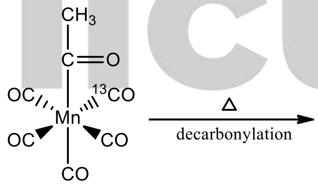
Since (bpy) ligand is rich in pi electrons its electronic movement is faster and hence outer sphere electron transfer reaction is faster.

In $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ the atomic configuration is $t_{2g}^4e_g^2$ and $t_{2g}^3e_g^2$ respectively. Electron transfer from $\pi^* \rightarrow \pi^*$, while in $[Co(NH_3)_6]^{2+/3+}$. One is high spin and later is low spin complex ($t_{2g}^5e_g^2$ and $t_{2g}^6e_g^0$) and electron transfers from $\pi^* \rightarrow \sigma^*$.

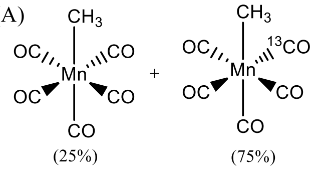
$\pi^* \rightarrow \pi^*$ electron transfer is faster than $\pi^* \rightarrow \sigma^*$ transfer, hence $k_{22} > k_{11} > k_{33}$.

[Correct option: B]

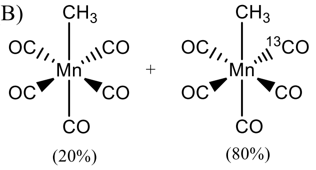
46. The CORRECT distribution of the products in the following reaction is



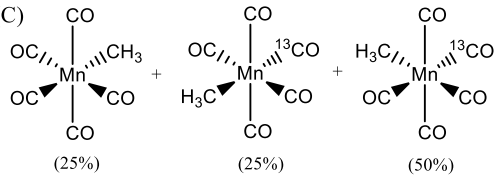
(A)



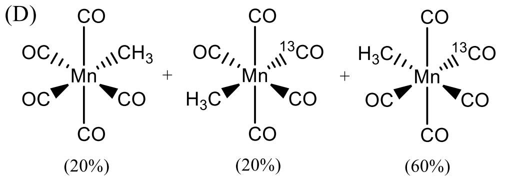
(B)



(C)

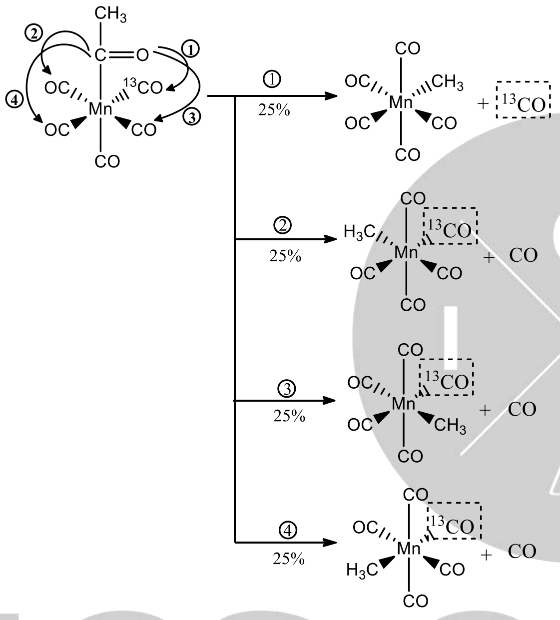


(D)



The solution

Decarbonylation follows cis manner only, so four choices are possible



- 3 & 4 are same, since ^{13}CO and CH_3 are cis to each other.
  So, ratio is 25: 25: 50

[Correct option: C]

47. The addition of $K_4[Fe(CN)_6]$ to a neutral aqueous solution of the cationic species of a metal produces a brown precipitate that is insoluble in dilute acid. The cationic species is

(A) Fe^{3+}	(B) UO_2^{2+}
(C) Th^{4+}	(D) Cu^{2+}

The solution

$$X^{n+} \xrightarrow{K[Fe(CN)_6]} \text{Brown precipitate}$$

cationic species insoluble in acid

$X^{n+} = ?$

Copper(II) give reddish brown ppt with $K_4[Fe(CN)_6]$ (potassium ferrocyanide).

$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$

therefore, answer is Cu^{2+}

[Correct option: D]

48. The electronic spectrum of a Ni(II) octahedral complex shows four d-d bands, labelled as P, Q, R, and S. Match the bands corresponding to the transitions.

	λ_{max}, $nm\ (\varepsilon, M^{-1}cm^{-1})$		Transitions
P	1000 (50)	I	$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(P)$
Q	770 (8)	II	$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(F)$
R	630 (55)	III	$^3A_{2g}(F) \longrightarrow {^3T_{2g}}(F)$
S	375 (110)	IV	$^3A_{2g}(F) \longrightarrow {^1E_g}(D)$

(A) P-IV, Q-III, R-II, S-I
(B) P-III, Q-IV, R-II, S-I
(C) P-II, Q-IV, R-I, S-III
(D) P-I, Q-IV, R-II, S-III

The solution

According to orgel diagram three transitions possible,

$^3A_{2g}(F) \longrightarrow {^3T_{2g}}(F)$ low energy
$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(F)$
$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(P)$ high energy

But here there is a low intensity band (lower ε value is given) that should be a forbidden transition $^3A_{2g}(F) \longrightarrow {^1E_g}(D)$

So,

$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(P) \Rightarrow S$
$^3A_{2g}(F) \longrightarrow {^3T_{2g}}(F) \Rightarrow P$
$^3A_{2g}(F) \longrightarrow {^3T_{1g}}(F) \Rightarrow R$
$^3A_{2g}(F) \longrightarrow {^1E_g}(D) \Rightarrow Q$

[Correct option: B]

49. In the following table, the left column represents the rigid-rotor type and the right column shows a set of molecules.

P. Symmetric rotor (oblate)	1. SiH_4
Q. Symmetric rotor (prolate)	2. CH_3Cl
R. Spherical rotor	3. C_6H_6
S. Asymmetric rotor	4. CH_3OH
	5. CO_2

The CORRECT match is
(A) P-1, Q-2, R-3, S-4
(B) P-3, Q-2, R-1, S-4
(C) P-3, Q-5, R-1, S-2
(D) P-5, Q-4, R-3, S-2

The solution

on the basis of moment of inertia, molecules are classified as

<i> spherical top
<ii> symmetric top
<iii> Asymmetric top
<iv> linear

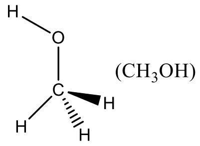
<i> spherical top
$I_A = I_B = I_C$
Molecules with point group
'T_d', 'O_h' and 'I_h'
Eg: CH_4, SF_6, IF_7 etc..

<ii> symmetric top
(a) Oblate symmetric top if $I_c > I_A = I_B$
Generally oblate symmetric tops are flat and round like a disc
Eg: C_6H_6, BH_3
(b) Prolate symmetric top
If $I_c = I_B > I_A$
In general, prolate symmetric ops are long and narrow (like a cigar)
Eg: CH_3-CH_3, CH_3I
NB: to confirm whether a molecule is oblate or prolate, explicit calculations of moment of inertia are needed.

<iii> Asymmetric top
$I_A \neq I_B \neq I_c$
Molecules like H_2O, Chlorobenzene
(both have C_{2v} point group)

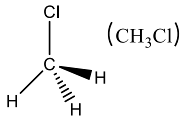
<iv> linear molecules
$I_C = I_B$; $I_A = 0$
Eg:- OCS, HBr, O_2 etc...
Then,
P-3
Q-2
R-1
S-4

Methanol



not a symmetric top

Chloromethane



prolate symmetric top

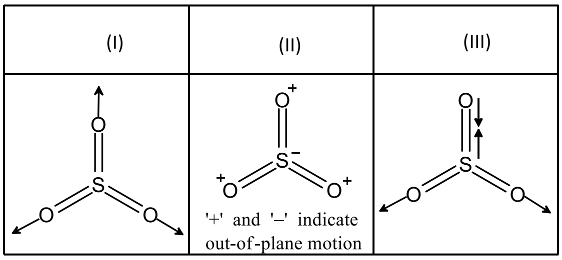
Carbon dioxide

O=C=O

linear

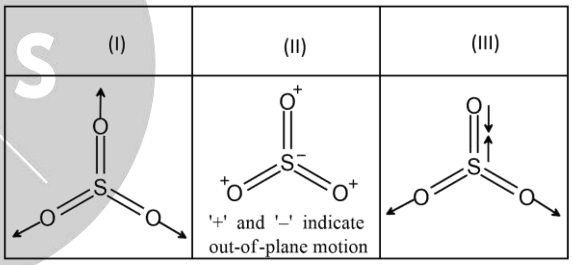
[Correct option: B]

50. The CORRECT statement regarding the following three normal modes of vibration of SO_3 is



(A) (I) and (II) are infrared active while (III) is infrared inactive.
(B) (I) is infrared inactive while (II) and (III) are infrared active.
(C) (I) and (III) are infrared inactive while (II) is infrared active.
(D) None of the modes are infrared active since SO_3 has zero dipole moment.

The solution

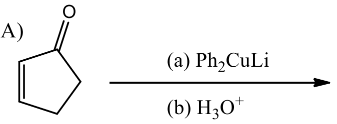


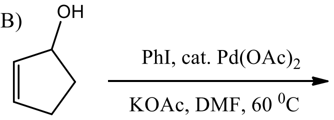
(I)	(II)	(III)
symmetric streching (does not change dipole moment) IR inactive	symetric deformation IR active 498 cm^{-1}	asymmetric stretching change in dipole moment IR active 1391 cm^{-1}

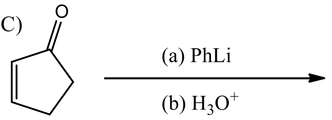
[Correct option: B]

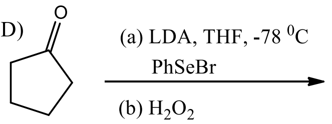
Q.51 – Q.56 (MSQ) Carry TWO mark each.

51. The reaction(s) that yield(s) 3-phenylcyclopentanone as the major product is(are)

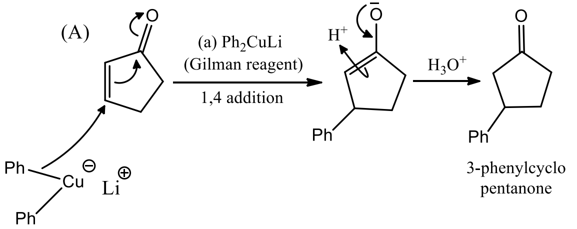
(A)


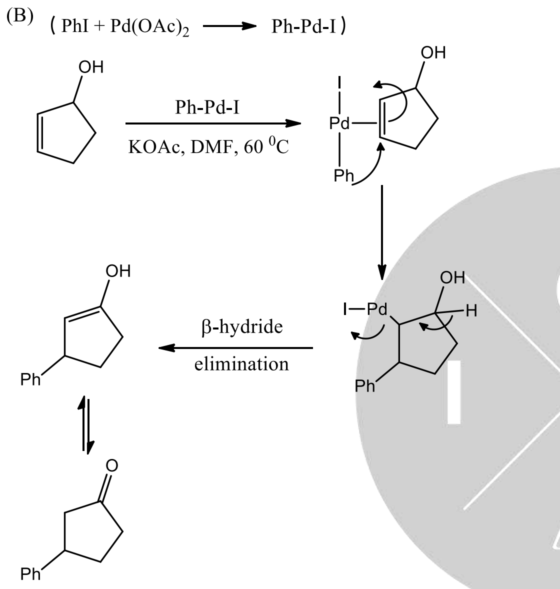
(B)


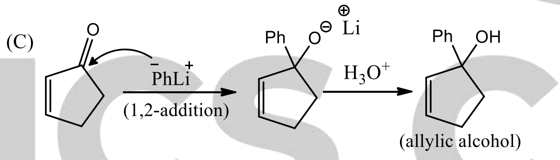
(C)


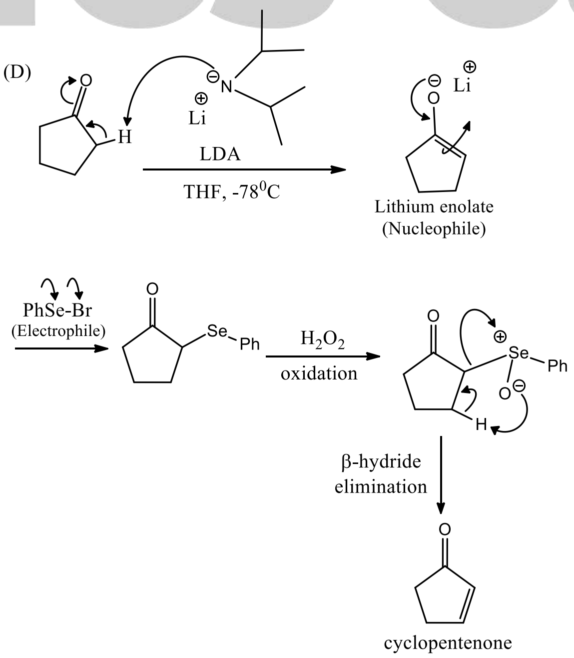
(D)


The solution



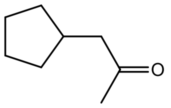




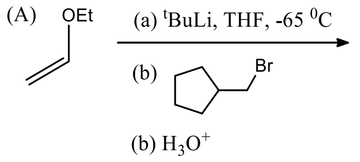


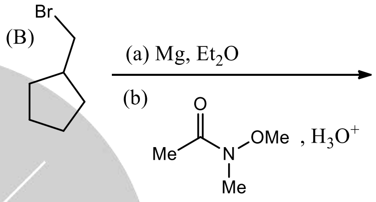
[Correct options: A & B]

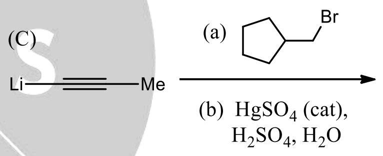
52. The reaction(s) that yield(s) **M** as the major product is(are)

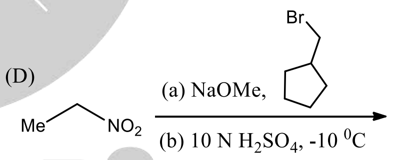


M

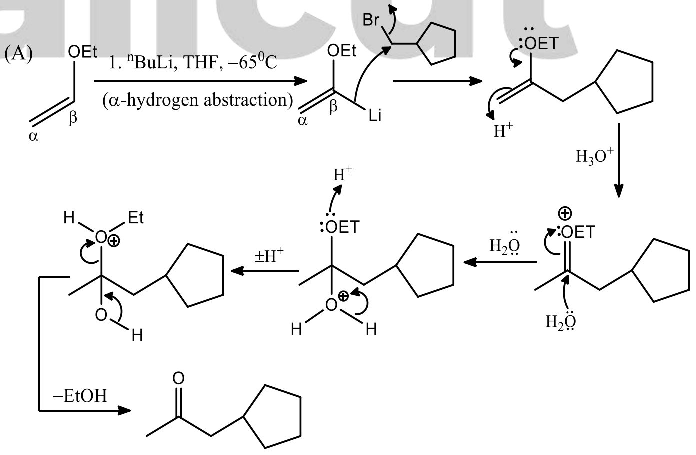


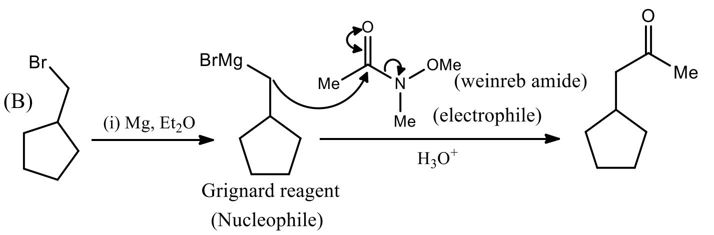


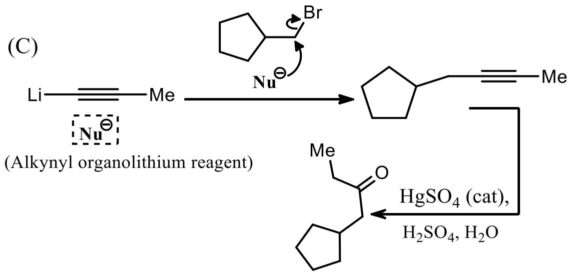


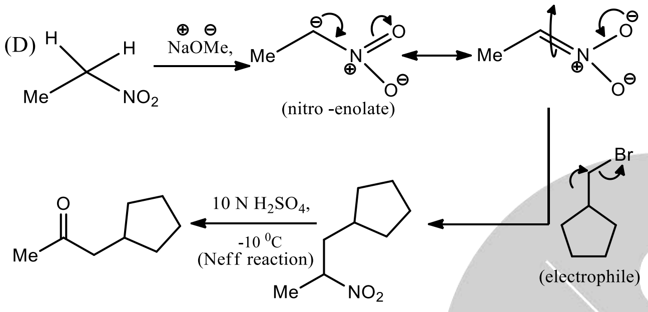


The solution









[Correct options: A, B & D]

53. The CORRECT statement(s) regarding $B_{10}H_{14}$ is(are)

(A) Brønsted acidity of $B_{10}H_{14}$ is higher than that of B_5H_9

(B) Structurally $B_{10}H_{14}$ is a closo-borane

(C) The metal-promoted fusion of $B_5H_8^-$ produces $B_{10}H_{14}$

(D) Both $B_{10}H_{14}$ and $B_{10}H_{12}(SEt_2)_2$ have the same number of valence electrons

The solution

- Increases the size of borane, acidity also increases.
- $B_{10}H_{14}$ = $B_{10}H_{10}^{4-}$ = $B_nH_n^{4-}$, ie. nido borane. (so, second statement is wrong)
- $$B_5H_8^- \xrightarrow{FeCl_2} B_{10}H_{14}$$
- $B_{10}H_{14} + 2\,SEt_2 \longrightarrow B_{10}H_{12}(SEt_2) + H_2$

[Correct options: A, C & D]

54. The CORRECT statement(s) about the Group-I metals is(are)

(A) Reactivity of Group-I metals with water decreases down the group

(B) Among the Group-Imetals, Li spontaneously reacts with N_2 to give a red-brownlayer-structured material

(C) Thermal stability of Group-I metal peroxides increases down the group

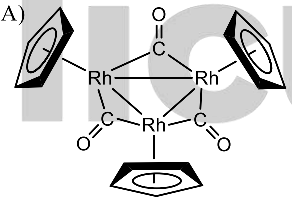
(D) All the Group-I metal halide are high-melting colorless crystalline solids

The solution

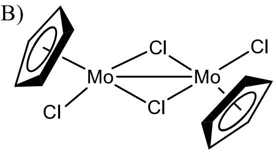
- Reactivity of Group-I metal with water decreases down the group. This statement is <u>wrong</u>.
  Reactivity of group-I metal increases down the group.
- Among group-I metal, Li spontaneously react with N_2 to give a red brown layer structured material is <u>right</u>.
  'Li' is the only alkali metal which react with N_2 (Li_3N- Reddish brown color).
- Thermal stability of Group-I metal peroxides increases down the group is <u>right</u>.
  Stability of peroxide or superoxide increases with the size of metal ion increases.
- All the Group-I metal halide are high-melting colorless crystalline solids. This statement is <u>right</u>.
  Alkali metal halides are prepared from M_2O, MOH, M_2CO_3 react with aqueous HX.
  [Correct options: B, C & D]

55. The compound(s) that satisfies/satisfy the 18-electron rule is(are)
(Atomic number of Os = 76, Rh = 45, Mo = 42, and Fe = 26)

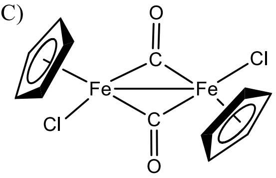
(A)



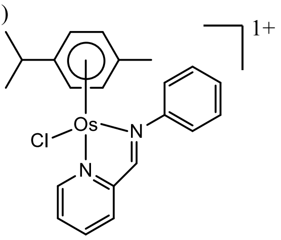
(B)



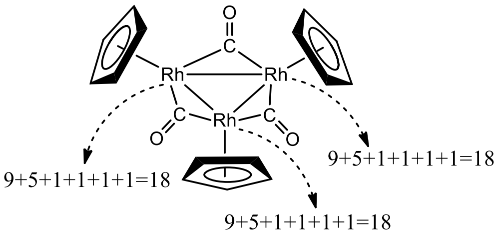
(C)

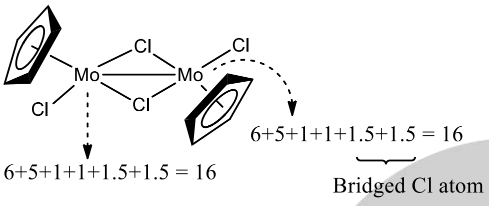


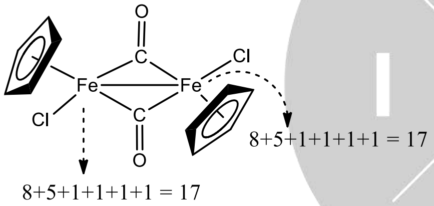
(D)

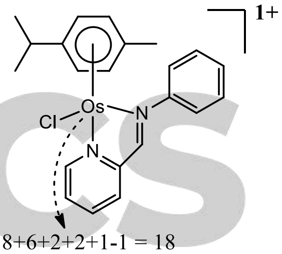


The solution









[Correct options: A & D]

56. For three operators $\hat{A}$, $\hat{B}$ and $\hat{C}$, $\left[\hat{A},\ [\hat{B},\hat{C}]\right] + \left[\hat{B},\ [\hat{C},\hat{A}]\right] =$

(A) $\left[\hat{C},\ [\hat{A},\hat{B}]\right]$

(B) $\left[\hat{C},\ [\hat{B},\hat{A}]\right]$

(C) $\left[[\hat{B},\hat{A}],\hat{C}\right]$

(D) $\left[[\hat{A},\hat{B}],\hat{C}\right]$

The solution

From Jacobi identity we get,

$$\left[\hat{A},[\hat{B},\hat{C}]\right] + \left[\hat{B},[\hat{C},\hat{A}]\right] + \left[\hat{C},[\hat{A},\hat{B}]\right] = 0$$

$$\left[\hat{A},[\hat{B},\hat{C}]\right] + \left[\hat{B},[\hat{C},\hat{A}]\right] = -\left[\hat{C},[\hat{A},\hat{B}]\right]$$

$$-\left[\hat{C},[\hat{A},B]\right] = -\left[\hat{C},[-\hat{B},\hat{A}]\right],$$

($[\hat{A},\hat{B}]$=$[-\hat{B},\hat{A}]$)

$$= \left[\hat{C},[\hat{B},\hat{A}]\right]$$

ie. 2nd option.

$$-\left[\hat{C},[\hat{A},B]\right] = -\left\{-\left[[\hat{A},\hat{B}],\hat{C}\right]\right\}$$

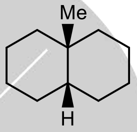
$$= \left[[\hat{A},\hat{B}],\hat{C}\right]$$

ie. 4th option.

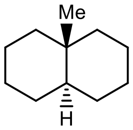
[Correct options: B & D]

Q.57 – Q.65 (NAT) Carry TWO mark each.

57. The difference between the number of Gauche-butane interactions present in **P** and **Q** is



P

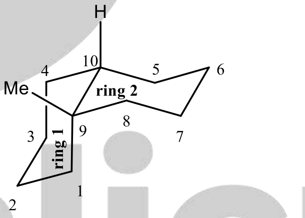


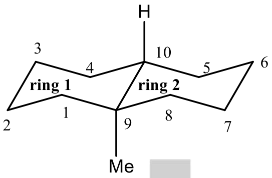
Q

The solution

P is cis 9-methyldecaline,

Q is trans 9-methyldecaline.





5-gauche butane interactions in P

1. C_1-C_9-C_8-C_7
2. C_1-C_9-C_{10}-C_5
3. C_3-C_4-C_{10}-C_5

4. and 5. are,

Methyl group is axial to ring 1. Therefore, an interaction with C_2 and C_4 carbon atoms.

4-gauche-butane interactions in Q

1. and 2. – methyl group is axial to ring-1, so with C_2 and C_4 carbon atoms.

3. and 4. also methyl group is axial to ring-2, so with C_5 and C_7 carbon atoms.

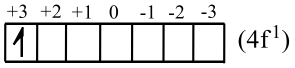
[Correct answer: 1 to 1]

58. The calculated magnetic moment (in BM, rounded off to two decimal places) of a Ce^{3+} complex is

The solution

Electronic configuration of cerium = [Xe] $4f^2\ 6s^2$

Electronic configuration of Ce^{3+} = [Xe] $4f^1\ 6s^0$



L = 3, S = 1/2

J = |L – S|, For orbital less than half filled
J = (3–1/2)= 5/2,

$$\therefore g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$= 1 + \frac{5/2\left(\frac{5}{2}+1\right) + 1/2\left(\frac{1}{2}+1\right) - 3(3+1)}{2 \times 5/2\left(\frac{5}{2}+1\right)}$$
$$= 6/7$$

The magnet moment of Ce^{3+} in B.M,

$$\therefore\ \mu_{eff} = g\sqrt{J(J+1)}$$

g = Lande splitting factor, here $g = 6/7$ and $J = 5/2$,

$$\mu_{eff} = 6/7\sqrt{5/2\left(\frac{5}{2}+1\right)}$$
$$= 6/7\sqrt{\frac{35}{4}}$$
$$= 6/7 \times \frac{\sqrt{35}}{2},$$
$$= 2.53$$

[Correct answer: 2.52 to 2.56]

59. The state of the electron in a He^+ ion is described by the following normalized wavefunction,

$$\Psi(r,\theta,\phi) = \sqrt{\frac{3}{8}}\, R_{21}(r)Y_{10}(\theta,\phi)$$
$$- i\sqrt{\frac{7}{16}}\, R_{10}(r)Y_{00}(\theta,\phi) + xR_{32}(r)Y_{20}(\theta,\phi).$$

Here, R_{nl} and Y_{lm} represent the radial and angular components of the eigenfunctions of He^+ ion, respectively, and x is an unknown constant. If the energy of the ion is measured in the above state, the probability (rounded off to two decimal places) of obtaining the energy of $-\frac{2}{9}$ atomic unit is

The solution

Given that

$$\Psi(r,\theta,\phi) = \sqrt{\frac{3}{8}}\, R_{21}(r)Y_{10}(\theta,\phi) - i\sqrt{\frac{7}{16}}\, R_{10}(r)Y_{00}(\theta,\phi)$$
$$+ xR_{32}(r)Y_{20}(\theta,\phi).$$

As a normalized wave function of He^+

$E_{total} = P_1E_1 + P_2E_2 + P_3E_3$

also $P_1 + P_2 + P_3 = 1$,

$P_1 = |C_1^2|$, $P_2 = |C_2^2|$, $P_3 = |C_3^2|$

$E_1 = -\frac{13.6\,Z^2}{n^2}$ ($Z = 2$, for He^+ and n = 2)

$= -\frac{13.6\times4}{4} = -13.6\ eV = -0.5\ au$ (au= atomic unit)

$E_2 = -\frac{13.6\,Z^2}{n^2}$ with ($Z = 2$ and n = 1)

$$= -\frac{13.6\times4}{1} = -2.0\ au$$

$E_3 = -\frac{13.6\,Z^2}{n^2}$ ($Z = 2$ and n = 3)

$$= -\frac{13.6\times4}{9} = -\frac{1}{9}\times(13.6\times4)$$
$$= -\frac{1}{9}\times 2$$
$$= -\frac{2}{9}\ au$$

The probability of obtaining the energy of $-\frac{2}{9}$ atomic unit is P_3.

$P_1 + P_2 + P_3 = 1$

$$\frac{3}{8} + \frac{7}{16} + x^2 = 1$$

$$x^2 = \frac{3}{16} = 0.187$$

[Correct answer: 0.18 to 0.20]

60. A certain wavefunction for the hydrogen-like atom is given by

$$\Psi(r,\theta,\phi) = \frac{2^{\frac{1}{2}}}{81\pi^{\frac{1}{2}}}\left(\frac{z}{a_0}\right)^{\frac{5}{2}}\left(6 - \frac{zr}{a_0}\right) r\, e^{-Zr/3a_0}\cos\theta.$$

The number of node(s) in this wavefunction is

The solution

$$\Psi(r,\theta,\phi) = \frac{2^{\frac{1}{2}}}{81\,\pi^{\frac{1}{2}}}\left(\frac{z}{a_0}\right)^{\frac{5}{2}}\left(6 - \frac{Zr}{a_0}\right) r\, e^{-Zr/3a_0}\cos\theta.$$

$$\boldsymbol{e^{-Zr/3a_0}}$$

'3' in above term indicate principal quantum number 'n'

Therefore, total node = n – 1,

ie, 3 – 1 = 2 (one radial node and one angular node)

[Correct answer: 2 to 2]

61. EMF of the following cell

Cu | $CuSO_4$(aq, 1.0 mol/kg) | Hg_2SO_4(s) | Hg(l) | Pt

at 25 ^{0}C and 1 bar is 0.36 V. The value of the mean activity coefficient (rounded off to three decimal places) of $CuSO_4$ at 25 ^{0}C and 1 bar is

[Given: Standard electrode potential values at 25 ^{0}C for
$Cu^{2+} + 2e^- \rightarrow Cu$ and
$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$
are 0.34 V and 0.62 V, respectively.
Consider: RT/F at 25 ^{0}C = 0.0256 V]

The solution

According to Nernst equation

$E_{cell} = E^{\theta}_{cell} - \frac{RT}{nF}\log_e Q$

Q = $\frac{\text{activity of product}}{\text{activity of reactant}}$

E_{cell} = potential of the cell

E^{θ}_{cell} = standard potential of the cell

According to IUPAC convention standard cell potential is considered to be standard reduction potential.

For the given cell.

Cu|CuSO$_4$(aq, 1 mol kg^{-1}) |Hg$_2$SO$_4$(s) |Hg(l) |Pt

Cell reactions are

Left

$Cu_{(S)} \rightarrow Cu^{2+} + 2\bar{e}$

Right

$Hg_2SO_4(s) + 2\bar{e} \rightarrow 2Hg_{(s)} + SO_4^{2-}{}_{(aq)}$

$E^{\theta}_{cell} = E^{\theta}_{right} - E^{\theta}_{left}$ (IUPAC convention)

(NB: Consider reduction potential on both sides)

$$E^{\theta}_{cell} = 0.62V - 0.34\ V = 0.28V$$

$$E_{cell} = E^{\theta}_{cell} - \frac{RT}{2F}\log_e\left(a_{SO_4^{2-}} \times a_{Cu^{2+}}\right)$$

$$a_{SO_4^{2-}} = a_{Cu^{2+}} \approx a_{\pm}$$

$$E_{cell} = E^{\theta}_{cell} - \frac{RT}{2F}\log_e(a_{\pm})^2$$

$$a_{\pm} = e^{\frac{E^{\theta}_{cell} - E_{cell}}{RT/F}} = e^{-3.125}$$

$= 0.0439 \approx 0.044$

[Correct answer: 0.042 to 0.046]

62. The radius of gyration (in nm, rounded off to one decimal place), for three dimensional random coil linear polyethylene of molecular weight 8,40,000 is

[Given: C–C bond length = 0.154 nm]

The solution

A random coil is a conformation of polymers the monomer subunits are oriented randomly while still being bonded to adjacent units. Radius of gyration (R$_g$) is the radius of hollow sphere that has the same rotational characteristics as the actual molecule.

For a three dimensional random coil

Radius of gyration, (R$_g$) = $\left[\frac{N}{6}\right]^{1/2} \times l$

N = total number of units

l = length of one unit

$$N = \frac{\text{total mass of all units}}{\text{mass of one unit}} = \frac{840000}{14}$$

$= 60000$

$$R_g = \left[\frac{60000}{6}\right]^{1/2} \times 0.154$$

$= [10000]^{1/2} \times 0.154$

$= 100 \times 0.154$ nm

$= 15.4$ nm

[Correct answer: 15.2 to 15.6]

63. The activation energy of the elementary gas-phase reaction $O_3 + NO \rightarrow NO_2 + O_2$ is 10.5 kJ mol^{-1}. The value of the standard enthalpy of activation (rounded off to two decimal places in kJ mol^{-1}) at 25 ^{0}C is

[Given: R is 8.314 J mol^{-1} K^{-1}]

The solution

For elementary (bimolecular) gas phase reaction like

$O_3 + NO \rightarrow NO_2 + O_2$

$\Delta^{\ddagger}H = E_a - 2RT$

(25^{0}C = 298 K)

$\Delta^{\ddagger}H$ = enthalpy of activation

E_a = energy of activation

R x T = 8.314 J K^{-1} mol^{-1} x 298 K

=2477.572 J mol^{-1}

= 2.478 J mol^{-1}

$\Delta^{\ddagger}H$ (in kJ mol^{-1}) = 10.5 – (2 x 2.478)

= 5.544

[Correct answer: 5.50 to 5.60]

64. In a collection of molecules, each molecule has two non-degenerate energy levels that are separated by 5000 cm^{-1}. On measuring the population at a particular temperature, it was found that the ground state population is 10 times that of the upper state. The temperature (in K, rounded off to the nearest integer) of measurement is

[Given: Value of the Boltzmann constant = 0.695 cm^{-1} K^{-1}]

The solution

From Boltzmann distribution of relative population,

$$\frac{N_u}{N_g} = \frac{g_u}{g_g}e^{-\Delta E/k_BT}, \Delta E = E_u - E_g$$

$u \longrightarrow$ upper state

$g \longrightarrow$ ground state

$g_u \longrightarrow$ degeneracy of upper state

$g_g \longrightarrow$ degeneracy of lower state

Since levels are non-degenerate

$$\frac{g_u}{g_g} = \frac{1}{1} = 1$$

$$ie. \quad \frac{N_u}{N_g} = e^{-\Delta E/k_BT},$$

$$log\left(\frac{N_u}{N_g}\right) = -\Delta E/k_BT$$

$$T = \frac{-\Delta E}{\left\{log_e\left(\frac{N_u}{N_g}\right)\right\} \times k_B}$$

$$\Delta E = 5000\ cm^{-1},\ k_B = 0.695\ cm^{-1}\ K^{-1}$$

$$N_u = 1, \quad N_g = 10$$

$$T = \frac{-5000\ cm^{-1}}{\left\{log_e\left(\frac{1}{10}\right)\right\} \times 0.695\ cm^{-1}\ K^{-1}}$$

$$= \frac{-5000}{\{-log_e\ 10\} \times 0.695}K$$

$$T = 3133.4\ K$$

[Correct answer: 3100 to 3150]

65. The change in entropy of the surroundings (in J K^{-1}, rounded off to two decimal places) to convert 1 mol of supercooled water at 263 K to ice at 263 K at 1 bar is
[Consider: $\Delta_{fus}H^0$ at 273 K = 6.0 kJ mol^{-1}, and the molar heat capacity of water is higher than that of ice by 37.0 J K^{-1} mol^{-1} in the temperature range of 263 K to 273 K]

The solution

Conversion of supercooled water to ice is a spontaneous process and spontaneous processes are necessarily irreversible.
For an irreversible isothermal process,

$$\Delta_{sur}S_{(263K)} = -\frac{\Delta_{sys}H_{(263K)}}{T}$$

sur = surrounding
sys= system
From Kirchhoff's law.

$$\Delta H_{(T_2)} = \Delta H_{(T_1)} + \Delta C_p \int_{T_1}^{T_2} dT$$

In given process,
$H_2O_{(l)}$ (263K) $\longrightarrow$ $H_2O_{(ice)}$ (263K)

$\Delta_{fus}H$ = 6 kJ mol^{-1} = 6000 J mol^{-1}

Then $\Delta_{freezing}H = -\Delta_{fus}H$
= –6000 J mol^{-1} (at 273 K)

$\Delta_{freezing}H\ (273K) = \Delta_{freezing}H\ (263K) + \Delta_r C_p (T_2 - T_1)$

$\Delta C_p = C_p(ice) - C_p(water)$
=–37 JK^{-1} mol^{-1}

Since C_p (water) = C_p (ice) + 37

$\Delta_{freezing}H(263K) = \Delta_{freezing}H(273K) - \Delta_r C_p (T_2 - T_1)$

= –6000–(–37 x 10)

$\Delta_{freezing}H(263K)$ = –5630 J mol^{-1} = $\Delta_{sys}H$ (263 K)

$$\Delta_{sur}S\ (263K) = -\frac{\Delta_{sys}H(263K)}{T}$$

$$= \frac{-(-5630)}{263} = 21.41$$

$\Delta_{sur}S$ (263K) = 21.41 J K^{-1} for 1 mol

[Correct answer: 21.20 to 21.60]

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