IITJEE–2006

Chemistry

Time: 2 hours

Note: Question number 1 to 12 carries (3, -1) ***marks*** each, 13 to 20 carries (5, -1) ***marks*** each, 21 to 32 carries (5, -2) ***marks*** each and 33 to 40 carries (6, 0) ***marks*** each.

Section – A (Single Option Correct)

1. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$

How can this reaction is made to proceed in forward direction?

(A) addition of cis 1, 2 diol
(B) addition of borax
(C) addition of trans 1, 2 diol
(D) addition of Na_2HPO_4

Sol. **(A)**

Due to formation of chelated complex, the reaction moves in forward direction.

2. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl/NH_4OH. the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4OH/NH_4Cl.

(A) $Zn(OH)_2$
(B) $Al(OH)_3$
(C) $Mg(OH)_2$
(D) $Ca(OH)_2$

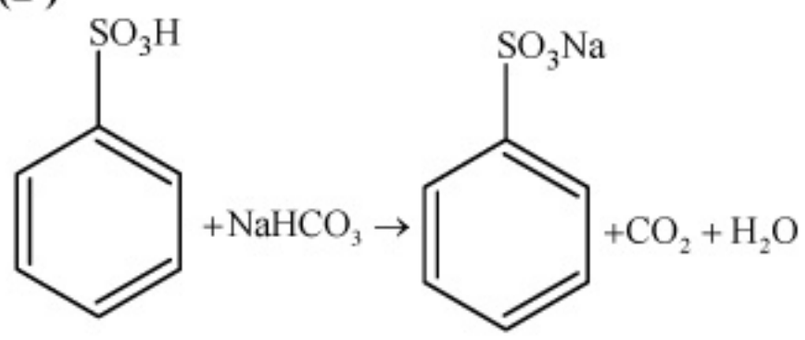
Sol. **(A)**

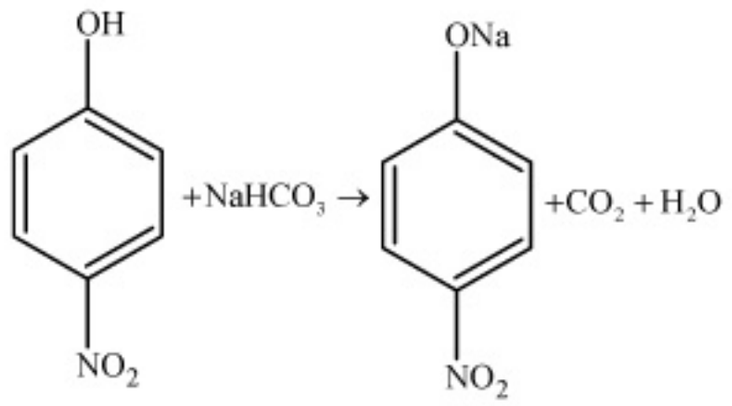
Due to formation of tetraammine zinc (II) complex; $Zn^{+2} + NH_4OH \rightarrow \left[Zn\left(NH_3\right)_4\right]^{+2}$

3. When benzene sulfonic acid and p-nitrophenol are treated with $NaHCO_3$, the gases released respectively are

(A) SO_2, NO_2
(B) SO_2, NO
(C) SO_2, CO_2
(D) CO_2, CO_2

Sol. **(D)**





4. A monatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

(A) $\frac{4R}{2}$
(B) $\frac{3R}{2}$
(C) 5R/2
(D) 0

Sol. **(A)**

5. (I) 1,2-dihydroxy benzene
(II) 1,3-dihydroxy benzene
(III) 1,4-dihydroxy benzene
(IV) Hydroxy benzene

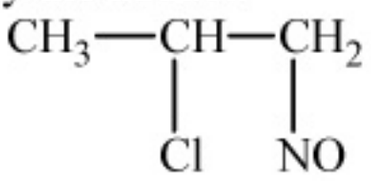
The increasing order of boiling points of above mentioned alcohols is

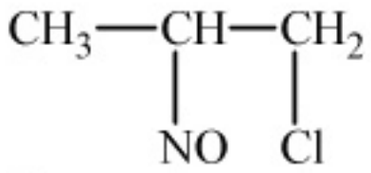
(A) I < II < III < IV
(B) I < II < IV < III
(C) IV < I < II < III
(D) IV < II < I < III

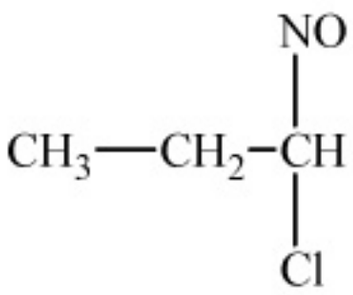
Sol. **(C)**

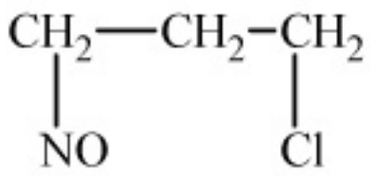
6. $CH_3\text{-}CH{=}CH_2 + NOCl \rightarrow P$

Identify the adduct.

(A) 

(B) 

(C) 

(D) 

Sol. **(A)**

$NOCl^- \rightarrow$ Markonikov's Addition

7. The IUPAC name of C_6H_5COCl is

(A) Benzoyl chloride
(B) Benzene chloro ketone
(C) Benzene carbonyl chloride
(D) Chloro phenyl ketone

Sol. **(C)**

8. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+];\ k_1 = 3.5\times10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ k_2 = 1.7\times10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is

(A) 6.08×10^{-6}
(B) 6.08×10^{6}
(C) 6.08×10^{-9}
(D) None

Sol. **(A)**

9. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O. Nitrogen containing compound is

(A) $CH_3\text{-}C{\equiv}N$
(B) $CH_3\text{-}NH\text{-}CH_3$
(C) $CH_3 - \overset{-}{N} \equiv \overset{+}{C}$
(D) $CH_3\overset{+}{N} \equiv \overset{-}{C}$

Sol. **(D)**

Isocyanide test/Carbylamine reaction

10. $CuSO_4$ decolourises on addition of KCN, the product is

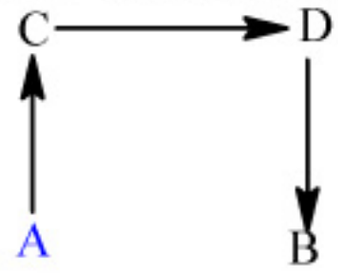
(A) $[Cu(CN)_4]^{2-}$
(B) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$
(C) $Cu(CN)_2$
(D) CuCN

Sol. **(D)**

$Cu^{+2} + 2CN^- \rightarrow Cu(CN)_2$

$2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2$

11. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:



Given $\Delta S_{(A\rightarrow C)} = 50$ e.u.

$\Delta S_{(C\rightarrow D)} = 30$ e.u.

$\Delta S_{(B\rightarrow D)} = 20$ e.u.

where e.u. is entropy unit

then $\Delta S_{(A\rightarrow B)}$ is

(A) +100 e.u.
(B) +60 e.u.
(C) −100 e.u.
(D) −60 e.u.

Sol. **(B)**

$$\Delta S_{(A\to B)} = \Delta S_{(A\to C)} + \Delta S_{(C\to D)} - \Delta S_{(B\to D)} = 50 + 30 - 20$$

12. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

(A) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

(C) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

(D) Catalyst will not alter the rate of either of the reaction.

Sol. **(B)**

Section – B (May have more than one option correct)

13. If the bond length of CO bond in carbon monoxide is $1.128\ \mathring{A}$, then what is the value of CO bond length in $Fe(CO)_5$?

(A) $1.15\ \mathring{A}$ (B) $1.128\ \mathring{A}$

(C) $1.72\ \mathring{A}$ (D) $1.118\ \mathring{A}$

Sol. **(A)**

Due to synergic bond formation between metal and CO, the bond order of CO decreases.

14. The species present in solution when CO_2 is dissolved in water are

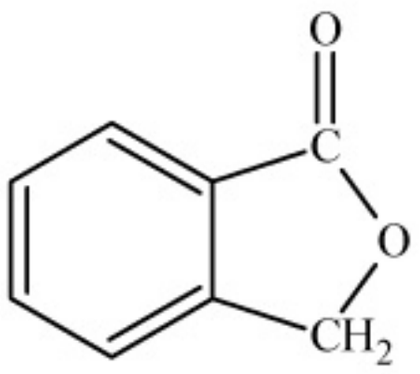
(A) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$ (B) H_2CO_3, CO_3^{2-}

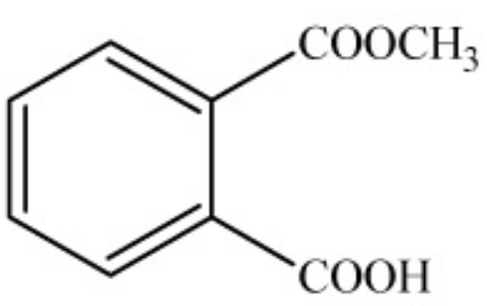
(C) CO_3^{2-}, HCO_3^- (D) CO_2, H_2CO_3

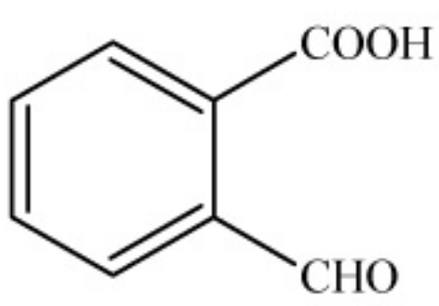
Sol. **(A)**

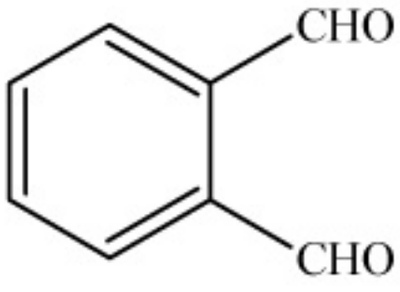
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$$

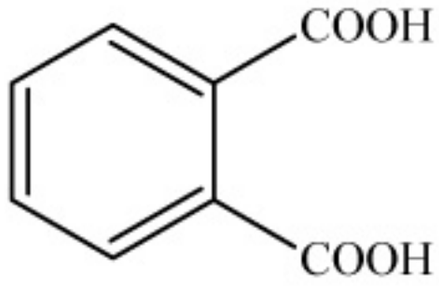
15. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product?



(A) 

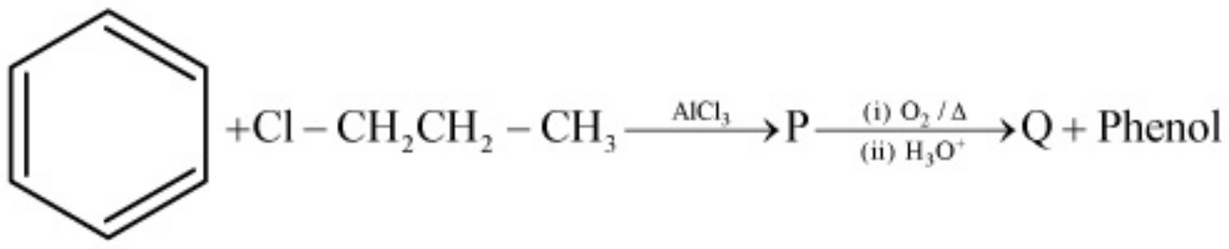
(B) 

(C) 

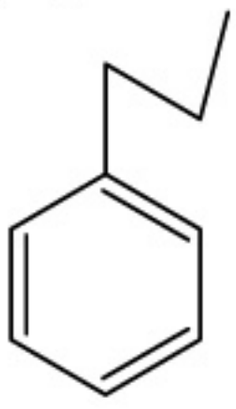
(D) 

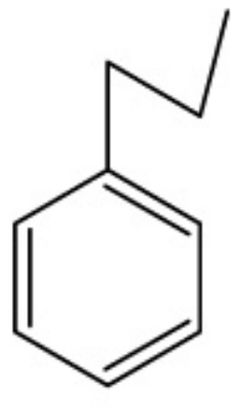
Sol. **(C)**

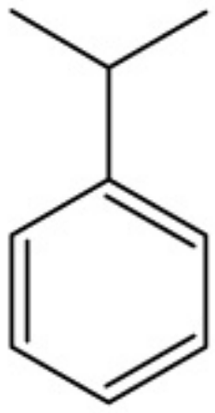
16.

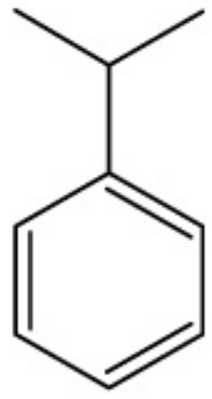


The major products P and Q are

(A)  and CH_3CH_2CHO

(B)  and CH_3COCH_3

(C)  and CH_3COCH_3

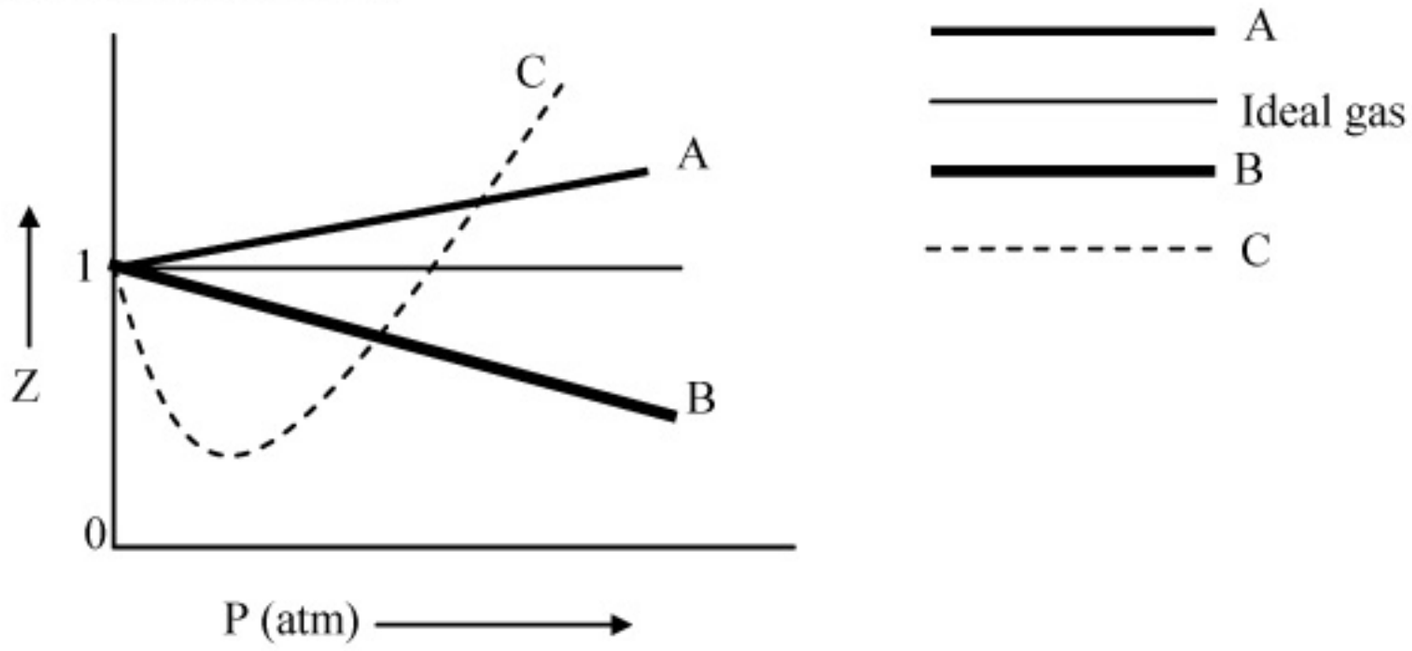
(D)  CH_3CH_2CHO

Sol. **(C)**

It is cumene hydroperoxide rearrangement reaction.

17. The given graph represents the variation of Z(compressibility factor $= \frac{PV}{nRT}$) versus P, for three real gases A, B and C.

Identify the only incorrect statement.



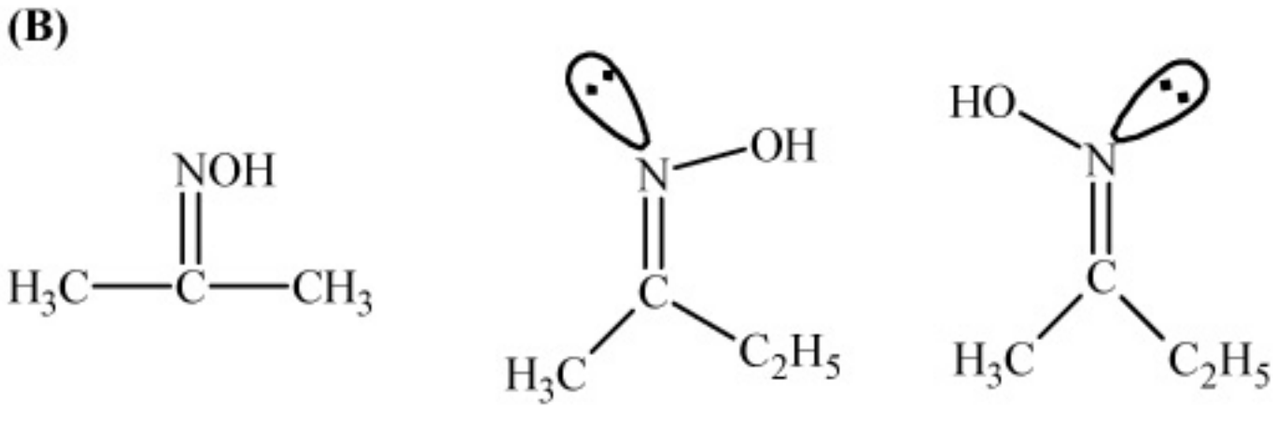
(A) For the gas A, a = 0 and its dependence on P is linear at all pressure.
(B) For the gas B, b = 0 and its dependence on P is linear at all pressure.
(C) For the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of intersection, with Z = 1, a and b can be calculated.
(D) At high pressure, the slope is positive for all real gases.

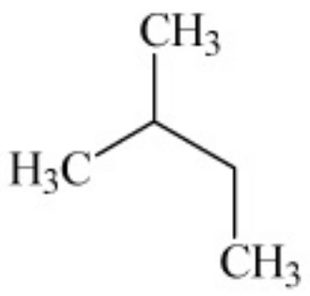
Sol. **(B)**

18. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime.

(A) Two different oximes are formed
(B) Three different oximes are formed
(C) Two oximes are optically active
(D) All oximes are optically active

Sol. **(B)**



19. 

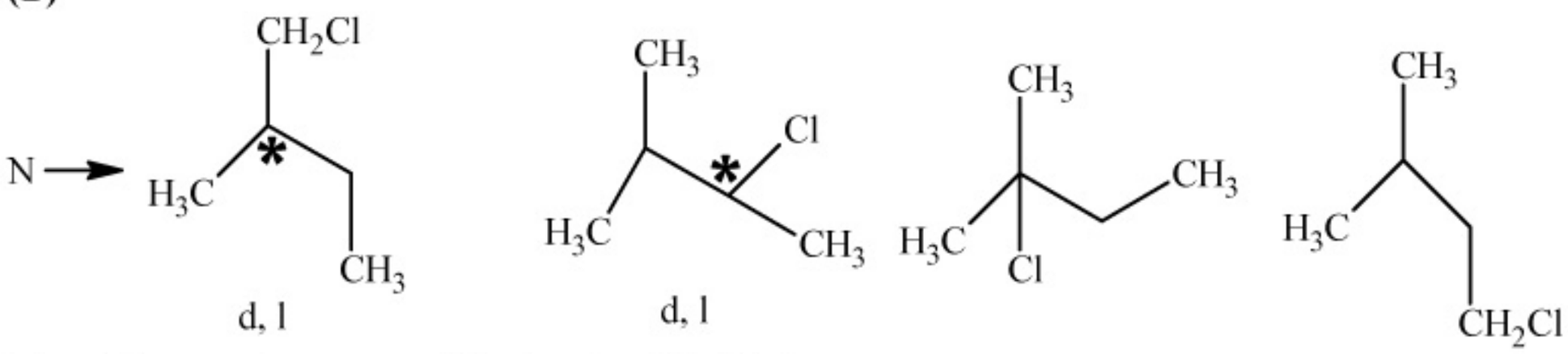
$\xrightarrow{Cl_2,\ h\nu}$ N (isomeric products) $C_5H_{11}Cl \xrightarrow{\text{fractional distillation}}$ M (isomeric products)

What are N and M?

(A) 6, 6 (B) 6, 4

(C) 4, 4 (D) 3, 3

Sol. **(B)**



M → d, l cannot be separated by fractional distillation.

20. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula?

(A) $Mg(NH_4)PO_4$ (B) $Mg_3(PO_4)_2$

(C) $MgCl_2.MgSO_4$ (D) $MgSO_4$

Sol. **(A)**

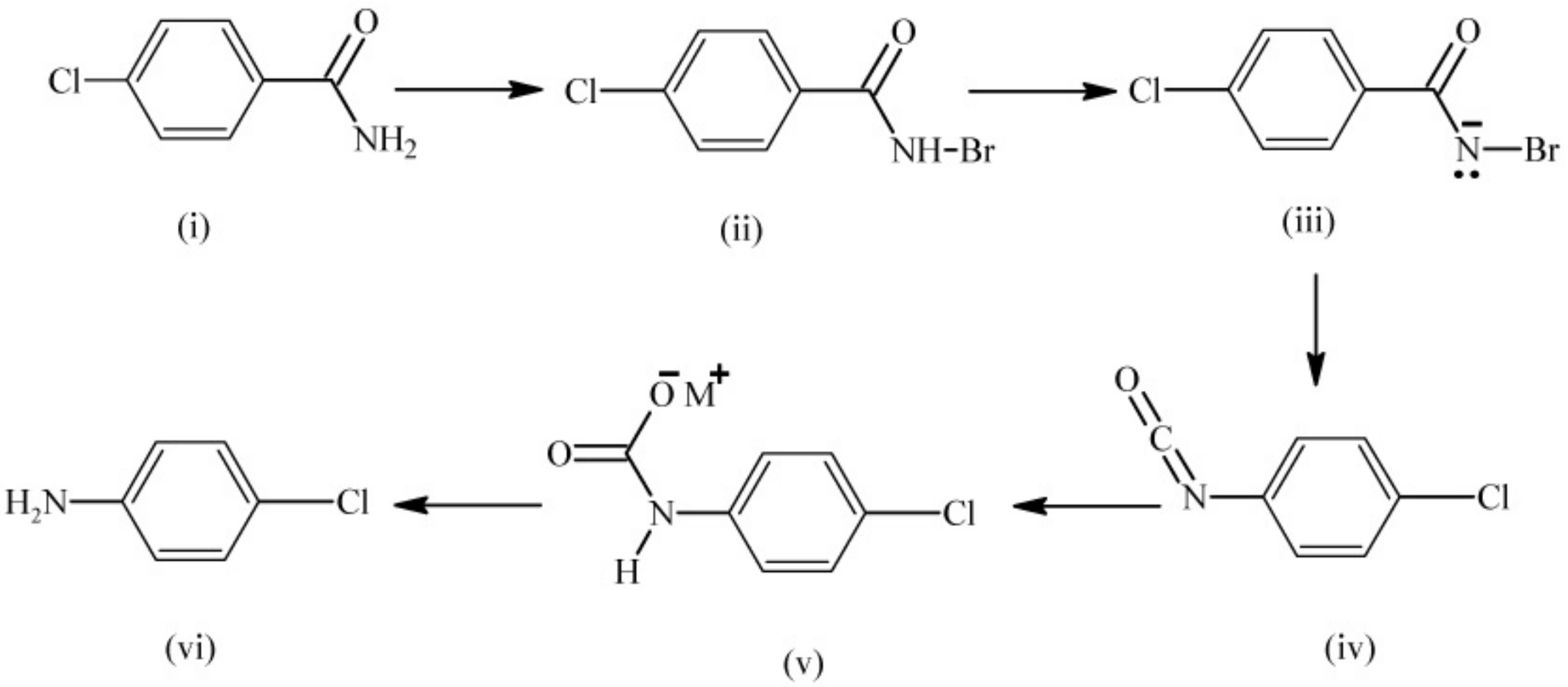
Test of Mg^{+2} ion

$$Mg^{+2} + NH_4OH + Na_2HPO_4 \rightarrow Mg(NH_4)PO_4$$

Section – C

Comprehension I

$RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

21. How can the conversion of (i) to (ii) be brought about?

(A) KBr (B) KBr + CH_3ONa

(C) KBr + KOH (D) Br_2 + KOH

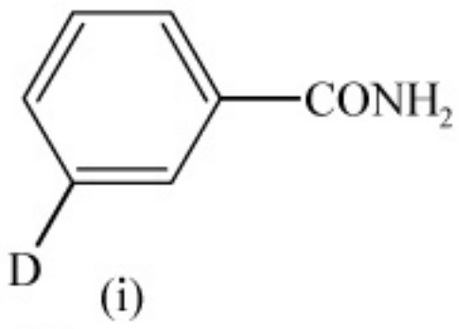
Sol. **(D)**

22. Which is the rate determining step in Hofmann bromamide degradation?

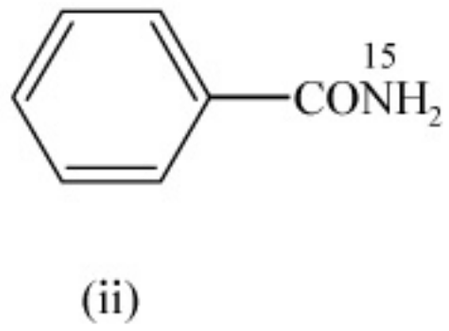
(A) Formation of (i)
(B) Formation of (ii)
(C) Formation of (iii)
(D) Formation of (iv)

Sol. **(D)**

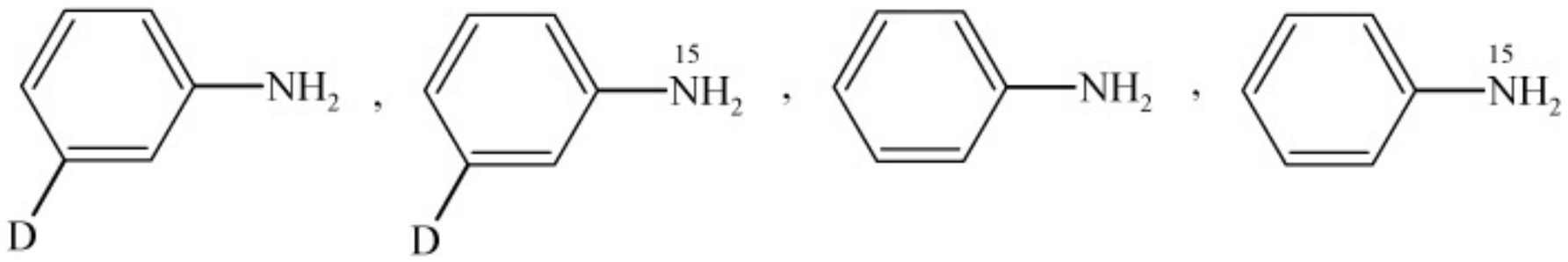
23. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?

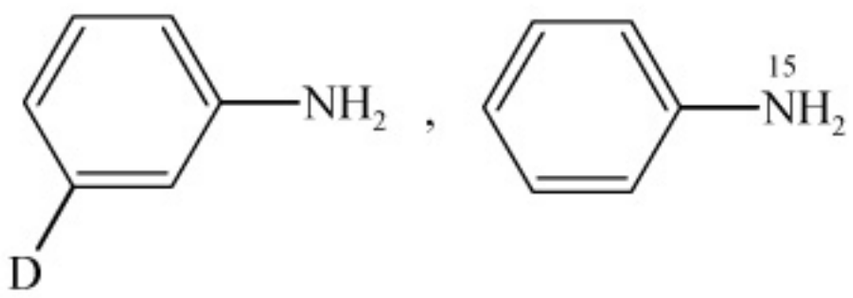


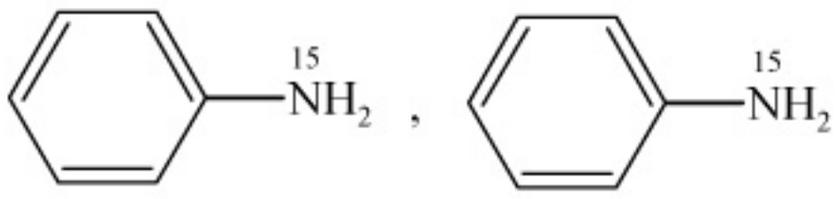
(i)

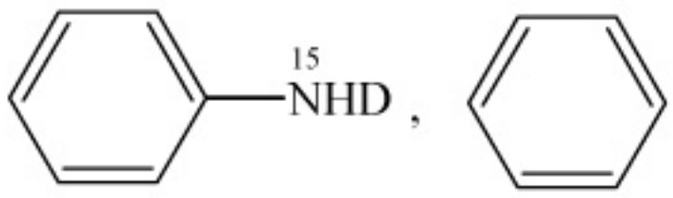


(ii)

(A) 

(B) 

(C) 

(D) 

Sol. **(B)**

Comprehension II

The coordination number of Ni^{2+} is 4.
$NiCl_2$ + KCN (excess) $\rightarrow$ A (cyano complex)
$NiCl_2$ + Conc. HCl (excess) $\rightarrow$ B (chloro complex)

24. The IUPAC name of A and B are

(A) Potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)
(B) Tetracyanopotassiumnickelate (II), teterachlorpotassiumnickelate (II)
(C) Tetracyanornickel (II), tetrachloronickel (II)
(D) Potassium tetracyanonickel (II), potassium tetrachloronickel (II)

Sol. **(A)**

25. Predict the magnetic nature of A and B.

(A) Both are diamagnetic.
(B) A is diamagnetic and B is paramagnetic with one unpaired electron.
(C) A is diamagnetic and B is paramagnetic with two unpaired electrons.
(D) Both are paramagnetic.

Sol. **(C)**

26. The hybridization of A and B are

(A) dsp^2, sp^3
(B) sp^3, sp^3
(C) dsp^2, dsp^2
(D) sp^3d^2, d^2sp^3

Sol. **(A)**

Comprehension III

Carbon – 14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N +_{0} n^{1} \rightarrow ^{14}_{6}C +_{1} n^{1}$$

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C^{14} undergoes

$$^{14}_{6}C \rightarrow ^{14}_{7}N + \beta^{-}$$

The half life period of ^{14}C is 5770 years. The decay constant (λ) can be calculated by using the following formula $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the β^{-} activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ^{14}C to ^{12}C in living matter is $1 : 10^{12}$.

27. Which of the following option is correct?
(A) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
(D) Carbon dating can not be used to determine concentration of ^{14}C in dead beings

Sol. **(C)**

28. What should be the age of fossil for meaningful determination of its age?
(A) 6 years
(B) 6000 years
(C) 60,000 years
(D) It can be used to calculate any age

Sol. **(B)**

29. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

(A) The age of the fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(B) The age of the fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(C) The age of fossil will be determined to be same

(D) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

Sol. **(A)**

Comprehension IV

Tollen's reagent is used for the detection of aldehyde when a solution of $AgNO_3$ is added to glucose with NH_4OH then gluconic acid is formed

$$Ag^{+} + e^{-} \rightarrow Ag;\ E^{\circ}_{red} = 0.8\ V$$

$$C_6H_{12}O_6 + H_2O \rightarrow \text{Gluconic acid}\left(C_6H_{12}O_7\right) + 2H^{+} + 2e^{-};\ E^{\circ}_{oxd} = -0.05\ V$$

$$Ag\left(NH_3\right)_2^{+} + e^{-} \rightarrow Ag(s) + 2NH_3;\ E^{\circ}_{red} = 0.337\ V$$

[Use $2.303 \times \frac{RT}{F} = 0.0592$ and $\frac{F}{RT} = 38.92$ at 298 K]

30. $2Ag^{+} + C_6H_{12}O_6 + H_2O \rightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^{+}$

Find ln K of this reaction.
(A) 66.13
(B) 58.38
(C) 28.30
(D) 46.29

Sol. **(B)**

$$E^{\circ}_{Cell} = \frac{RT}{nF}\ln K$$

$$(0.8-0.05) = \frac{1}{2}\times\frac{0.0592}{2.303}\ln K$$

$$\ln K = \frac{(0.8-0.05)\times 2\times 2.303}{0.0592} = 58.38$$

31. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

(A) E_{oxd} will increase by a factor of 0.65 from E°_{oxd} (B) E_{oxd} will decrease by a factor of 0.65 from E°_{oxd}

(C) E_{red} will increase by a factor of 0.65 from E°_{red} (D) E_{red} will decrease by a factor of 0.65 from E°_{red}

Sol. **(A)**

On increasing concentration of NH_3, the concentration of H^+ ion decreases. Therefore, E_{red} increases.

32. Ammonia is always is added in this reaction. Which of the following must be incorrect?

(A) NH_3 combines with Ag^+ to form a complex.

(B) $Ag(NH_3)_2^+$ is a stronger oxidising reagent than Ag^+.

(C) In absence of NH_3 silver salt of gluconic acid is formed.

(D) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

Sol. **(D)**

Section – D

33. 75.2 g of C_6H_5OH(phenol) is dissolved in a solvent of $K_f = 14$. If the depression in freezing point is 7 K then find the % of phenol that dimerises.

Sol.

$$\underset{C-C\alpha}{2C_6H_5OH} \rightleftharpoons \underset{\frac{C\alpha}{2}}{(C_6H_5OH)_2}$$

$$7 = 14\times 0.8\left(\frac{2-\alpha}{2}\right)$$

$\alpha = 0.75 =$ **75%**

34. For the reaction, $2CO + O_2 \longrightarrow 2CO_2$; $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.
(1 L atm = 0.1 kJ)

Sol.

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + V\Delta P$$

$$\Delta U = \Delta H - V\Delta P = -560 + 1\times 30\times 0.1$$

$$= -557$$

Absolute value = **557 kJ**

35. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units.
Given, $\lambda^{\circ}_{(Ag^+)} = 6\times 10^{-3}\ Sm^2\,mol^{-1}$, $\lambda^{\circ}_{(Br^-)} = 8\times 10^{-3}\ Sm^2\,mol^{-1}$, $\lambda^{\circ}_{(NO_3^-)} = 7\times 10^{-3}\ Sm^2\,mol^{-1}$.

Sol. The solubility of AgBr in presence of 10^{-7} molar $AgNO_3$ is 3×10^{-7} M.

Therefore $[Br^-] = 3\times 10^{-4}\ m^3$, $[Ag^+] = 4\times 10^{-4}\ m^3$ and $[NO_3^-] = 10^{-4}\ m^3$

Therefore $\kappa_{total} = \kappa_{Br^-} + \kappa_{Ag^+} + \kappa_{NO_3^-} =$ **55 Sm^{-1}**

36. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm.

Sol. $$\rho = \frac{ZA}{NV}$$

$$Z = \frac{\rho NV}{A} = \frac{2 \times 6 \times 10^{23} \times \left(5 \times 10^{-8}\right)^3}{75}$$

$n = 2$

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 5 = 2.165 \text{ Å} = \mathbf{216.5 \text{ pm}}$$

Note: Answer may be 216 pm or 217 pm.

Section – E

37. Match the extraction processes listed in Column I with metals listed in Column II:

	Column I		**Column II**
(A)	Self reduction	(P)	Lead
(B)	Carbon reduction	(Q)	Silver
(C)	Complex formation and displacement by metal	(R)	Copper
(D)	Decomposition of iodide	(S)	Boron

Sol. **A – P,R; B – P,R; C – Q; D – S**

38. Match the following:

	Column I		**Column II**
(A)	$Bi^{3+} \longrightarrow (BiO)^+$	(P)	Heat
(B)	$[AlO_2]^- \longrightarrow Al(OH)_3$	(Q)	Hydrolysis
(C)	$SiO_4^{4-} \longrightarrow Si_2O_7^{6-}$	(R)	Acidification
(D)	$(B_4O_7^{2-}) \longrightarrow [B(OH)_3]$	(S)	Dilution by water

Sol. **A – Q; B – R; C – P; D – Q,R**

39. According to Bohr's theory,
E_n = Total energy
K_n = Kinetic energy
V_n = Potential energy
r_n = Radius of n^{th} orbit
Match the following:

	Column I		**Column II**
(A)	$V_n/K_n = ?$	(P)	0
(B)	If radius of n^{th} orbit $\propto E_n^x$, $x = ?$	(Q)	–1
(C)	Angular momentum in lowest orbital	(R)	–2
(D)	$\frac{1}{r^n} \propto Z^y$, $y = ?$	(S)	1

Sol. **A– R; B – Q; C – P; D – S**

40. Match the following:

	Column I		**Column II**
(A)	CH_3–CHBr–CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	(P)	E1 reaction
(B)	Ph – CHBr - CH_3 reacts faster than Ph-CHBr-CD_3.	(Q)	E2 reaction
(C)	Ph-CH_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	(R)	E1cb reaction
(D)	$PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(S)	First order reaction

Sol. **A – Q; B – Q; C – R,S; D – P,S**