JEE (ADVANCE) - 2016
CHEMISTRY

SECTION 1 (Maximum Marks: 18)

- This section contains **SIX** questions
- Each question has FOUR option (A), (B), (C) and (D). **ONLY ONE** of these four option is correct.
- For each question, darken the bubble corresponding to the correct option(s) in the ORS.
- For each question, marks will be awarded in one of the following categories:

  Full Marks : +3 If only the bubble corresponding to the correct answer is darkened.

  Zero Marks : 0 If none of the bubbles is darkened.

  Negative Marks : –1 In all other cases.

19. For the following electrochemical cell at 298 K,

$$Pt(s) | H_2(g, 1bar) | H^+(aq, 1M) || M^{4+}(aq), M^{2+}(aq) | Pt(s)$$

$$E_{cell} = 0.092V \text{ when } \frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$$

Given : $E^0_{M^{4+}M^{2+}} = 0.151V; 2.303\frac{RT}{F} = 0.059V$

The value of x is

(A) –2 (B) –1 (C) 1 (D) 2

Key (D)

Sol: $H_2 + M^{4+} \rightarrow 2H^+ + M^{2+}$

$$E_{cell} = 0.151 - \frac{0.059}{2}\log\frac{[M^{2+}][H^+]^2}{[M^{4+}]}$$

$$\Rightarrow 0.092 = 0.151 - \frac{0.059}{2}\log\frac{[M^{2+}]}{[M^{4+}]}$$

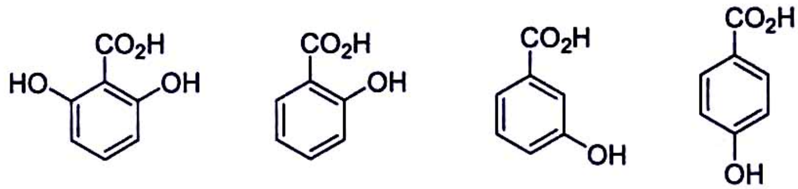
$$\Rightarrow -.059 = -\frac{0.059}{2}\log\frac{[M^{2+}]}{[M^{4+}]}$$

$$\Rightarrow \log\frac{[M^{2+}]}{[M^{4+}]} = 2$$

$$\Rightarrow \frac{[M^{2+}]}{[M^{4+}]} = 10^2$$

$\therefore x = 2$

20. The correct order of acidity for the following compounds is



I II III IV

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

Key (A)

Sol: Due to ortho effect

II is more acidic than

III and IV

21. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively, are

(A) octahedral, square planar and tetrahedral (B) square planar, octahedral and tetrahedral

(C) tetrahedral, square planar and octahedral (D) octahedral, tetrahedral and square planar

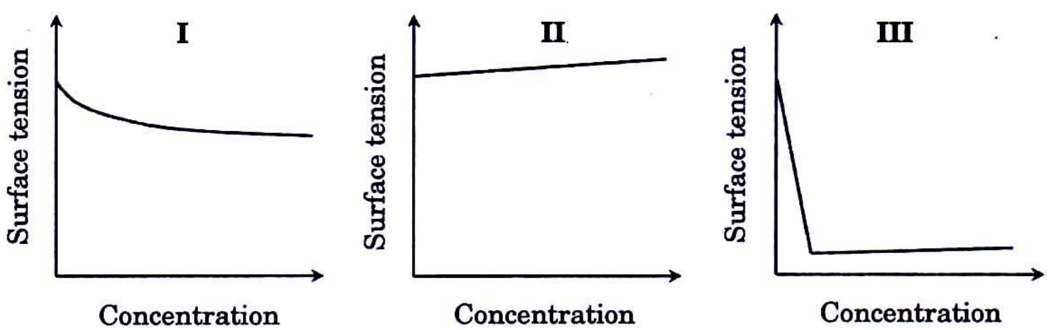
Key (A)

Sol: $\left[Ni(NH_3)_6\right]^{+2}$ Octahedral

$\left[Pt(NH_3)_4\right]^{+2}$ Square Planar

$\left[Zn(NH_3)_4\right]^{+2}$ Tetrahedral

22. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solution of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-$ Na^+ at room temperature. The correct assignment of the sketches is



(A) I : KCl II : CH_3OH III: $CH_3(CH_2)_{11}OSO_3^-Na^+$

(B) I : $CH_3(CH_2)_{11}OSO_3^-Na^+$ II : CH_3OH III : KCl

(C) I : KCl II : $CH_3(CH_2)_{11}OSO_3^-Na^+$ III : CH_3OH

(D) I : CH_3OH II : KCl III : $CH_3(CH_2)_{11}OSO_3^-Na^+$

Key (D)

Sol: organic solvents decreases surface tension, electrolytes increases it partially. Surfactant drastically reduces the surface tension .

23. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\text{Clear solution}}{X} \xrightarrow{Ag^+} \underset{\text{white precipitate}}{Y} \xrightarrow{\text{With time}} \underset{\text{Black precipitate}}{Y}$$

(A) $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S (B) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3, Ag_2S

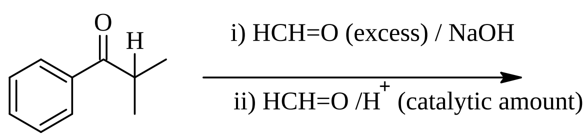
(C) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag (D) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4, Ag

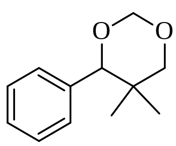
Key (A)

Sol: $$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\text{Clear solution}}{\left[Ag\left(S_2O_3\right)_2\right]^{3-}} \xrightarrow{Ag^+} \underset{\text{white precipitate}}{Ag_2S_2O_3} \xrightarrow{\text{With time}} \underset{\text{Black precipitate}}{Y}$$

$$Ag_2S_2O_3H_2O \rightarrow Ag_2S + H_2SO_4$$

24. The major product of the following reaction sequence is



(A)


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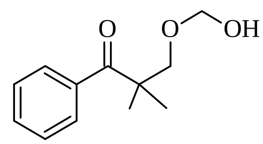

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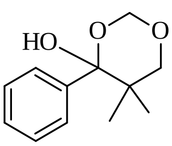
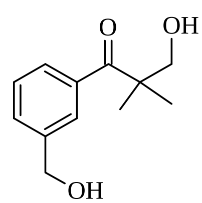
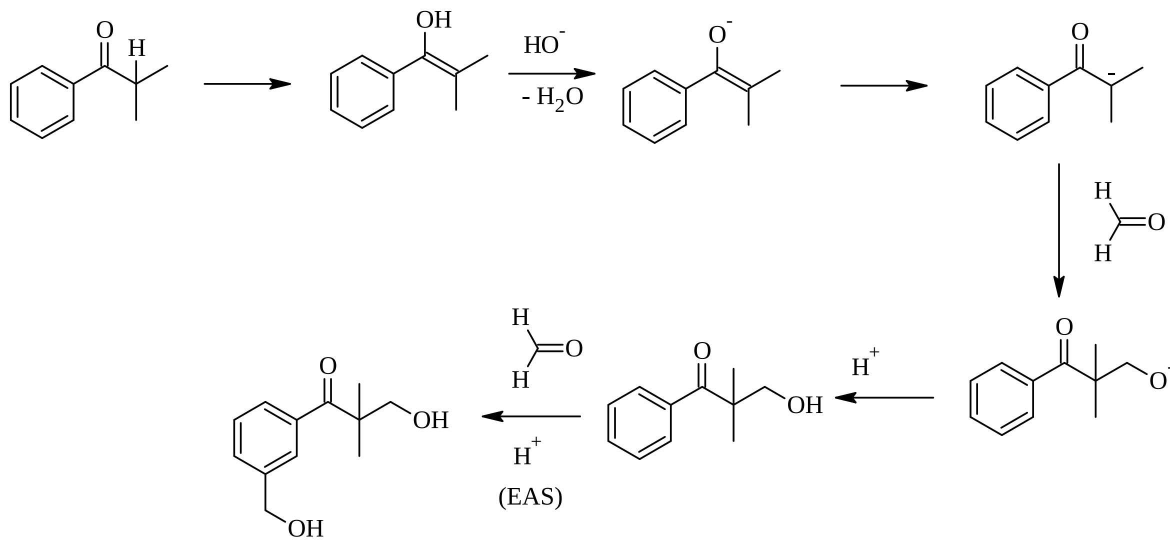


(D)


Key (D)

Sol:


SECTION 2 (Maximum Marks: 18)

- This section contains **EIGHT** questions
- Each question has Four options (A), (B), (C) and (D) ONE OR MORE THAN ONE of these four option(s) is (are) correct.
- For each question, marks will be awarded in one of the following categories :

  Full Marks : +4 if only the bubble(s) corresponding to all the correct option(s) is (are) darkened.

  Zero Marks : 0 if none of the bubbles is darkened.

  Negative Marks : –2 in all other cases
- For example, if (A), (C) and (D) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (A) and (D) will result in +2 marks; and darkening (A) and (B) will result in -2 marks, as a wrong option is also darkened.

25. For "invert sugar" the correct statement(s) is (are)

(Given: specific rotations of (+)-sucrose, (+)-maltose, L-(-)-glucose and L-(+)-fructose in aqueous solution are $+66^0$, $+140^0$, $+66^0$, -52^0, and $+92^0$, respectively)

(A) invert sugar is prepared by acid catalyzed hydrolysis of maltose

(B) invert sugar is an equimolar mixture of D-(+)glucose and D-(+)-fructose

(C) specific rotation of invert sugar is -20^0

(D) on reaction with Br_2 water, invert sugar forms saccharic acid as one of the products

Key (B, C)

Sol: Sucrose on hydrolysis gives equimolar mixture of glucose and fructose called invert sugar. The optical rotation of hydrolysis products are $+ 52.5^0$ and -92.8^0. The resulting rotation of the solution is -20^0.

26. mixture(s) showing positive deviation from Raoult's law at 35^o is (are)

(A) carbon tetrachloride + methanol

(B) carbon disulphide + acetone

(C) benzene + toluene

(D) phenol + aniline

Key (A, B)

Sol: The intermolecular forces (hydrogen bonds in methanol) become weaker when carbon tetrachloride is added into methanol which results into positive deviation.

The intermolecular forces become weaker when CS_2 (non-polar) is added into acetone (polar) which results into positive deviation.

Benzene and toluene forms form ideal solution

Phenol and acetone leads to show negative deviation

27. The **CORRECT** statement(s) for cubic close (ccp) three dimensional structure is(are)

(A) the number of nearest neighboring of an atom present in the topmost layer is 12

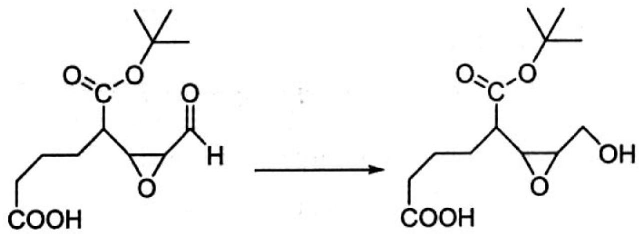
(B) the efficiency of atom packing is 74%

(C) the number of octahedral and tetrahedral voids per atom are 1 and 2 respectively

(D) thw unit cell edge length is $2\sqrt{2}$ times the radius of the atom

Key (B, C, D)

28. Reagent(s) which can be used to bring about the following transformation is (are)



(A) $LiAlH_4$ in $(C_2H_5)_2O$

(B) BH_3 in THF

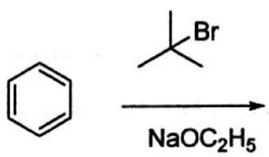
(C) $NaBH_4$ in C_2H_5OH

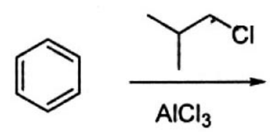
(D) Raney Ni/H_2 in THF

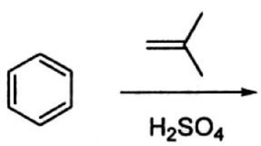
Key (C)

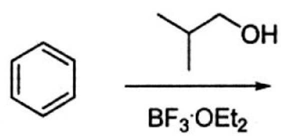
Sol: $NaBH_4$ in C_2H_5OH will reduce only aldehyde group in given structure to form desired product.

29. Among the following, reaction(s) *tert*-butyl benzene as the major product is (are)

(A) 

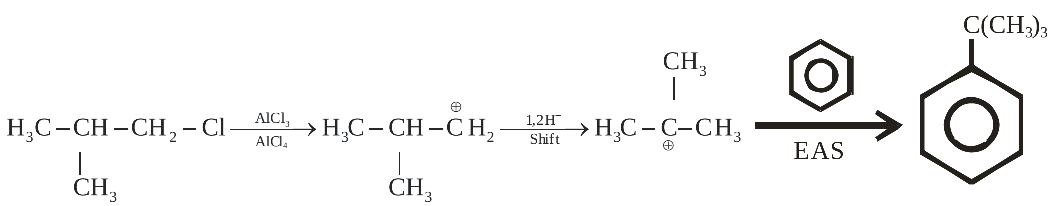
(B) 

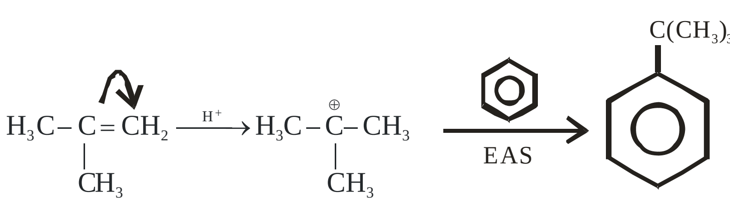
(C) 

(D) 

Key (B, C, D)

Sol:





$\Rightarrow$ In $BF_3.OEt_2$ alcohol will give carbocation

30. Extraction of copper from copper pyrite ($CuFeS_2$) involves

(A) crushing followed by concentration of the ore by froth flotation

(B) removal of iron as slag

(C) self-reduction step to produce ‘Blister copper’ following evolution of SO_2

(D) refining of ‘blister copper’ by carbon reduction

Key (A, B, C)

Sol: $\underset{\text{copper pyrite}}{CuFeS_2} \xrightarrow{\text{Crushed}} \text{concentration by froth floatation method}$

$CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + \underset{\text{Flux}}{SiO_2} \longrightarrow FeSiO_3\,(\text{slag})$

$2Cu_2O + Cu_2S \xrightarrow[\text{reduction}]{\text{Auto}} \underbrace{6Cu}_{\text{Blister-copper}} + SO_2$

31. According to Molecular Orbital Theory,

(A) C_2^{2-} is expected to be diamagnetic

(B) O_2^{2+} is expected to have a longer bond length than O_2

(C) N_2^{+} and N_2^{-} have same bond order

(D) He_2^{+} has the same energy as two isolated He atom

Key (A, C)

Sol: $\underset{(14e^-)}{C_2^{2-}}$ $\sigma 1s^2\, \sigma^* 1s^2, \sigma 2s^2\, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$\therefore$ It is diamagnetic

$\underset{(14e^-)}{O_2^{2-}}$ $\sigma 1s^2\, \sigma^* 1s^2, \sigma 2s^2\, \sigma^* 2s^2, \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$

$\therefore$ Bond order = 3

Whereas O_2 has bond order = 2

$\therefore$ O_2^{2+} has less bond length than O_2

$\underset{(13e^-)}{N_2^{+}}$ $\sigma 1s^2\, \sigma^* 1s^2, \sigma 2s^2\, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \pi 2p_z^1$

$\therefore$ Bond order = (9–4)/2 = 2.5

$\underset{(15e^-)}{N_2^{-}}$ $\sigma 1s^2\, \sigma^* 1s^2, \sigma 2s^2\, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \pi 2p_z^2$

$\therefore$ Bond order= (10–5)/2 = 2.5

He_2^{+} has bond order = 0.5

$\therefore$ It has different energy than two isolated He atom

32. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

(A) can also be prepared by reaction of P_4 and HNO_3

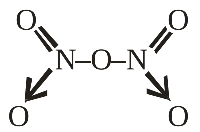
(B) is diamagnetic

(C) contains one N-N bond

(D) reacts with Na metal producing a brown gas

Key (B, D)

Sol: $HNO_3 + P_4O_{10} \rightarrow N_2O_5 + HPO_3$



$N_2O_5 \xrightarrow{Na} NaNO_3 + \underset{Brown}{NO_2} \uparrow$

Section 3 (Maximum Marks : 12)

- This section contains **TWO** paragraph.
- Based on each paragraph, there are **TWO** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question darken the bubble corresponding to the correct option in the ORS.
- For each question marks will e awarded in one of the following categories

Full marks : +3 If only the bubble corresponding to the correct option is darkened.

Zero marks: 0 In all other cases

COMPREHENSIVE

PARAGRAPH 1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equations

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^o$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X as the reaction proceed the number of moles of X formed is given by β. Thus $\beta_{equilbrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.(Given : R= 0.083 L bar $K^{-1}mol^{-1}$

33. The equilibrium K_P for this reaction at 298 K, in terms of $\beta_{equilbrium}$, is

(A) $\dfrac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$

(B) $\dfrac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

(C) $\dfrac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$

(D) $\dfrac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

Key (B)

Sol: $x_2(g) \rightleftharpoons 2\times(g)$

$$x_2(g) \rightleftharpoons 2\times(g)$$

$t=0$	1	0
$t=t_{eq}$	$1-\alpha$	2α

$2\alpha = \beta_{eq}$

$\Rightarrow 4\alpha^2 = (\beta_{eq})^2 \ldots(i)$

$$k_p = \frac{\left(\frac{2\alpha}{1+\alpha}.P_t\right)^2}{\left(\frac{1-\alpha}{1+\alpha}.P_t\right)} = \left(\frac{4\alpha^2}{1-\alpha^2}\right)(P_t)$$

$$K_P = \frac{8\beta_{eq}^2}{4-(\beta_{eq})^2}$$

Hence Ans. B

34. The **INCORRECT** statement among the following for this reaction, is

(A) Decrease in the total pressure will result in formation of more moles of gaseous X

(B) At the start of the reaction, dissociation of gaseous X_2 takes places spontaneously

(C) $\beta_{equilibrium} = 0.7$

(D) $K_C < 1$

Key (C)

Sol: As pressure decrease equilibrium shift towards more number of moles as $\Delta G^o > 0$ reaction is nonspontaneous & we know that

as $\Delta, G^o \to -RT\ln(K_C)$

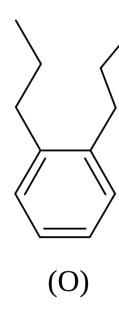
As $\Delta G^\circ \to +ve$

K_C should be < 1

Hence incorrect statement is (C)

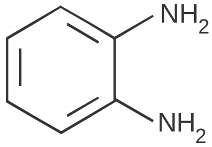
PARAGRAPH 2

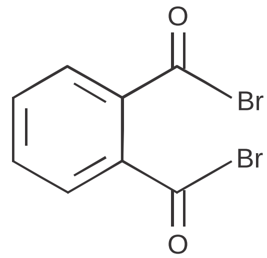
Treatment of compound **O** with $KMnO_4/\overset{+}{H}$ gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with $Br_2/NaOH$ produced **R**. On strong heating **Q** gave **S**, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification gave a compound **T**.

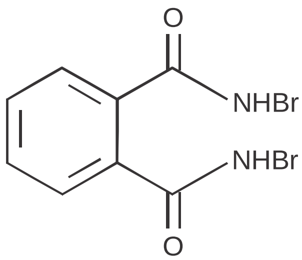


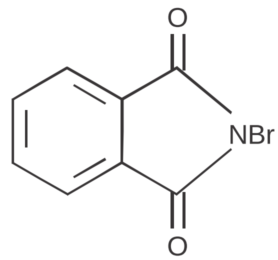
(O)

35. The compound **R** is

(A) 

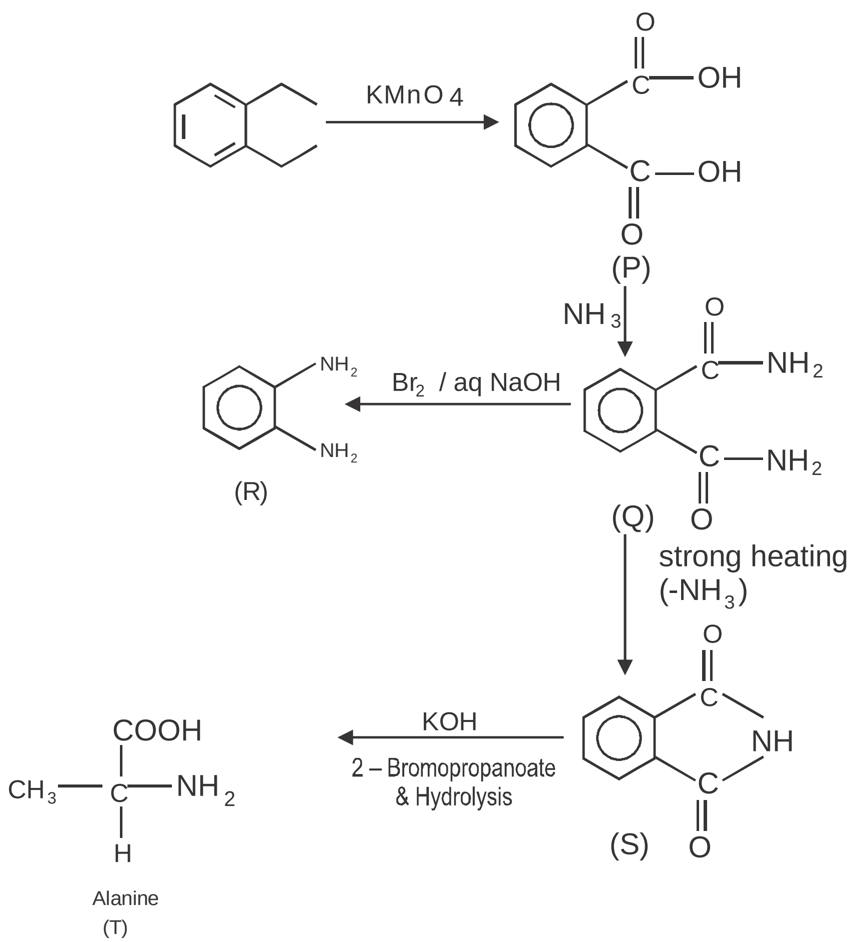
(B) 

(C) 

(D) 

Key (A)

Sol:



36. The compound **T** is

(A) Glycine
(B) alanine
(C) valine
(D) serine

Key (B)

Sol: From the above (Q. 35) solution