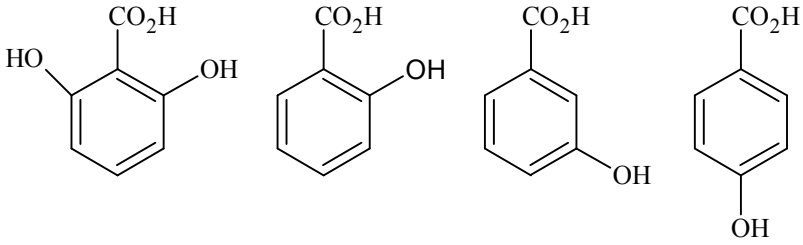
PART II : CHEMISTRY

SECTION 1 (Maximum Marks: 18)

- This section contains **SIX** 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 be awarded in one of the following categories:

  Full Marks : +3 If only the bubble corresponding to the correct option is darkened
  Zero Marks : 0 If none of the bubbles is darkened
  Negative Marks : –1 In all other cases

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

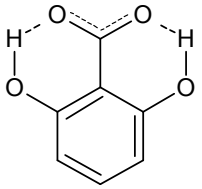


I II III IV

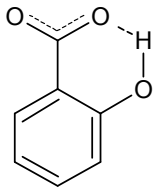
(A) I > II > III > IV (B) III > I > II > IV
(C) III > IV > II > I (D) I > III > IV > II

Sol. **(A)**

Stabler the conjugate base stronger the acid.



Conjugate base stabilized by intramolecular H-bond from both the sides.



Conjugate base stabilized by intramolecular H-bond from one side.

20. 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

Sol. **(A)**

$$\underset{\text{octahedral}}{\left[Ni(NH_3)_6\right]^{2+}};\ \underset{\text{square planar}}{\left[Pt(NH_3)_4\right]^{2+}};\ \underset{\text{tetrahedral}}{\left[Zn(NH_3)_4\right]^{2+}}$$

21. For the following electrochemical cell at 298 K,

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

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

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

The value of *x* is

(A) –2 (B) –1

(C) 1 (D) 2

Sol. **(D)**

Anode : $H_2 - 2e \rightleftharpoons 2H^+$

Cathode : $M^{4+} + 2e \rightleftharpoons M^{2+}$

Net cell reaction : $H_2 + M^{4+} \rightleftharpoons 2H^+ + M^{2+}$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\frac{\left[H^+\right]^2\left[M^{2+}\right]}{\left[M^{4+}\right]\times P_{H_2}}$$

$$0.092 = 0.151 - \frac{0.059}{2}\log 10^x$$

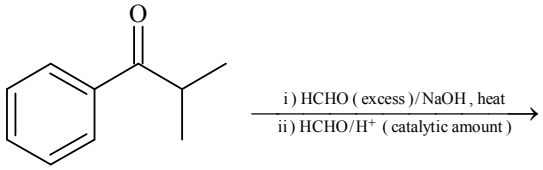
$$0.092 = 0.151 - \frac{0.059}{2}x$$

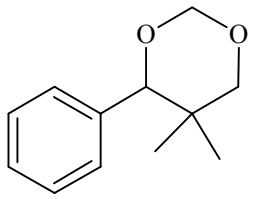
$$\frac{0.059\,x}{2} = 0.151 - 0.092$$

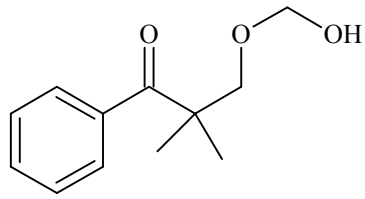
$0.059\ x = 0.059 \times 2$

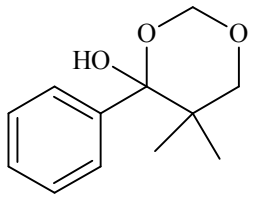
$x = 2$

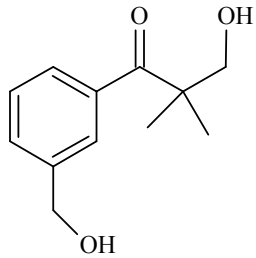
22. The major product of the following reaction sequence is



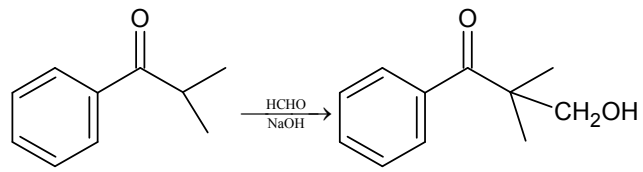
(A) 

(B) 

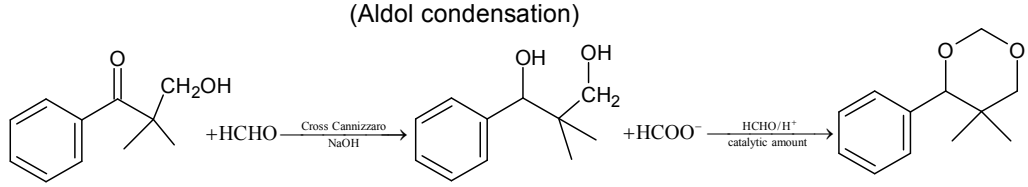
(C) 

(D) 

Sol. **(A)**



(Aldol condensation)



(acetal formation)

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

$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\text{clear solution}}{X} \xrightarrow{Ag^+} \underset{\text{white precipitate}}{Y} \xrightarrow{\text{with time}} \underset{\text{black precipitate}}{Z}$$

(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) $[Ag(SO_3)_2]^{3-}, Ag_2S_2O_3, Ag$

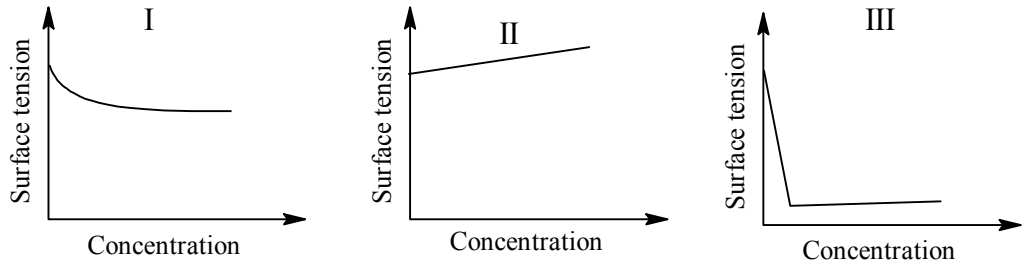
(D) $[Ag(SO_3)_3]^{3-}, Ag_2SO_4, Ag$

Sol. **A**

$$Ag^+ + 2S_2O_3^{2-} \longrightarrow \underset{\text{X (clear solution)}}{\left[Ag(S_2O_3)_2\right]^{3-}} \xrightarrow{Ag^+} \underset{\text{Y (white)}}{Ag_2S_2O_3} \xrightarrow{\text{with time}} \underset{\text{Z (black)}}{Ag_2S}$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

24. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions 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 : $CH_3(CH_2)_{11}OSO_3^-Na^+$

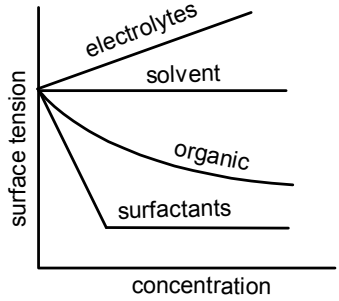
(B) I : $CH_3(CH_2)_{11}OSO_3^-Na^+$ II : CH_3OH III : KCl

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

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

Sol. **(D)**

Strong electrolytes like KCl increase the surface tension slightly. Low molar mass organic compounds usually decrease the surface tension. Surface active organic compounds like detergents sharply decrease surface tension



SECTION 2 (Maximum Marks: 32)

- 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, darken the bubble(s) corresponding to all the correct option(s) in the ORS
- For each question, marks will be awarded in <u>one of the following categories</u>:

  Full Marks : +4 If only the bubble(s) corresponding to all the correct option(s) is (are) darkened
  Partial Marks : +1 For darkening a bubble corresponding to each correct option, provided NO incorrect option is 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.

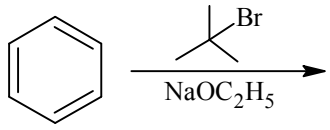
25. For 'invert sugar', the correct statement(s) is(are)
(Given: specific rotations of (+)-sucrose, (+)-maltose, L-(–)-glucose and L-(+)-fructose in aqueous solution are +66º, +140º, –52º and +92º, respectively)
(A) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose
(B) 'invert sugar' is an equimolar mixture of D-(+)-glucose and D-(–)-fructose
(C) specific rotation of 'invert sugar' is –20º
(D) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

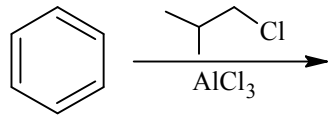
Sol. **(B, C)**

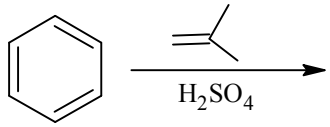
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\substack{D-(+)-glucose\\ +52^0}}{C_6H_{12}O_6} + \underset{\substack{D-(-)-fructose\\ -92^0}}{C_6H_{12}O_6}$$

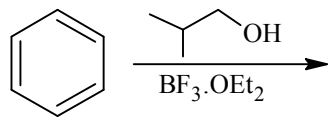
$$\alpha_{\text{invert sugar}} = \frac{+52^0 - 92^0}{2} = -20^0 \text{ (average is taken as both monomers are one mole each)}$$

*26. Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are)

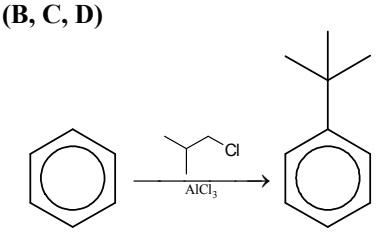
(A) 

(B) 

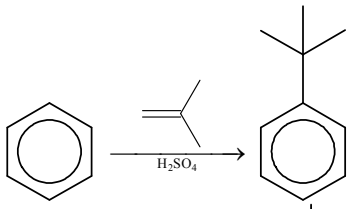
(C) 

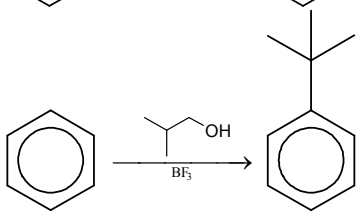
(D) 

Sol. **(B, C, D)**



via rearrangement of carbocation





via rearrangement of carbocation

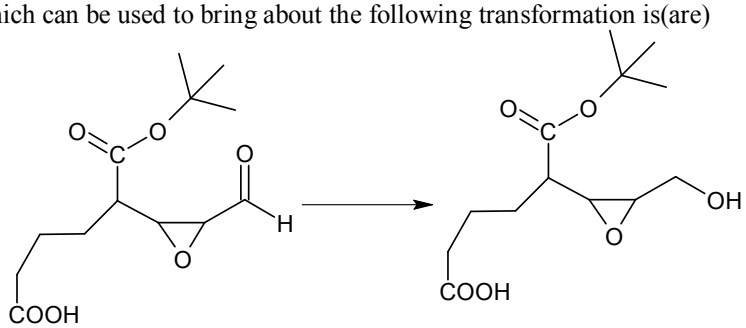
27. Extraction of copper from copper pyrite ($CuFeS_2$) involves
(A) crushing followed by concentration of the ore by froth flotation
(B) removal of iron as slag
(C) self-reduction step to produce 'blister copper' following evolution of SO_2
(D) refining of 'blister copper' by carbon reduction

Sol. **(A, B, C)**
Refining of blister copper is done by poling technique.

28. The CORRECT statement(s) for cubic close packed (*ccp*) three dimensional structure is(are)
(A) The number of the nearest neighbours 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) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

Sol. **(B, C, D)**
The middle layers will have 12 nearest neighbours. The top-most layer will have 9 nearest neighbours.
$4r = a\sqrt{2}$, where 'a' is edge length of unit cell and 'r' is radius of atom.

29. 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

Sol. **(C, D)**
$NaBH_4$ and Raney Ni/H_2 do not react with acid, ester or epoxide entities of an organic compound.

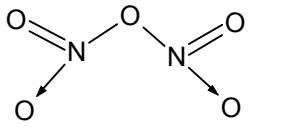
30. Mixture (s) showing positive deviation from Raoult's law at 35°C is (are)
(A) carbon tetrachloride + methanol (B) carbon disulphide + acetone
(C) benzene + toluene (D) phenol + aniline

Sol. **(A, B)**
Benzene + toluene will form ideal solution.
Phenol + aniline will show negative deviation.

31. 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

Sol. **(B, D)**

$$2HNO_3 \xrightarrow[(\text{dehydration},\ -H_2O)]{P_4O_{10}} N_2O_5$$



$$Na + N_2O_5 \longrightarrow NaNO_3 + \underset{(\text{brown})}{NO_2}\uparrow$$

*32. According to Molecular Orbital Theory
(A) C_2^{2-} is expected to be diamagnetic
(B) O_2^{2+} expected to have a longer bond length than O_2
(C) N_2^+ and N_2^- have the same bond order
(D) He_2^+ has the same energy as two isolated He atoms

Sol. **(A, C)**

SECTION 3 (Maximum Marks: 12)

- This section contains **TWO** paragraphs
- Based on each paragraph, there will be **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(s) corresponding to the correct option 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 all the correct option is darkened
  Zero Marks : 0 In all other cases.

PARAGRAPH 1

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

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

The standard reaction Gibbs energy, $\Delta_r G^0$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilibrium}$ 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 constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is

(A) $\frac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (B) $\frac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

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

Sol. **(B)**

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

$$1$$

$$1-\frac{\beta_e}{2} \qquad \beta_e$$

Total number of moles at equilibrium.

$$\Rightarrow 1-\frac{\beta_e}{2}+\beta_e$$

$$\Rightarrow 1+\frac{\beta_e}{2}$$

$$K_p = \frac{(p_x)^2}{p_{x_2}}$$

$$= \frac{\left(\frac{\beta_e \times 2}{1+\frac{\beta_e}{2}}\right)^2}{\frac{\left(1-\frac{\beta_e}{2}\right)\times 2}{1+\frac{\beta_e}{2}}}$$

$$= \frac{2\beta_e^2}{1-\frac{\beta_e^2}{4}}$$

$$K_p = \frac{8\beta_e^2}{4-\beta_e^2}$$

*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 place spontaneously

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

(D) $K_c < 1$

Sol. **(C)**

There is no data given to find the $\beta_{equilibrium}$ exact value.

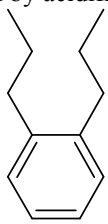
$$\Delta G_c^0 = -2.303RT \log K_c$$

$$\log K_c = -1$$

$$K_c < 1$$

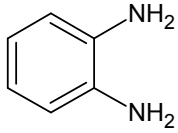
PARAGRAPH 2

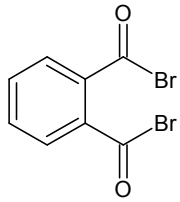
Treatment of compound **O** with $KMnO_4/H^+$ gave **P**, which on heating with ammonia gave **Q.** The compound **Q** on treatment with Br_2/NaOH produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification,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

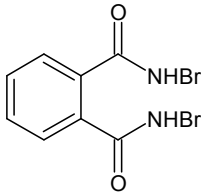


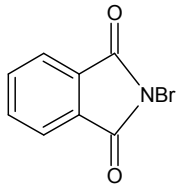
[O]

35. The compound **R** is

(A) 

(B) 

(C) 

(D) 

Sol. **(A)**

36. The compound **T** is

(A) glycine (B) alanine

(C) valine (D) serine

Sol. **(B)**

35&36.