PART II: CHEMISTRY

SECTION 1 [Maximum Marks: 21]

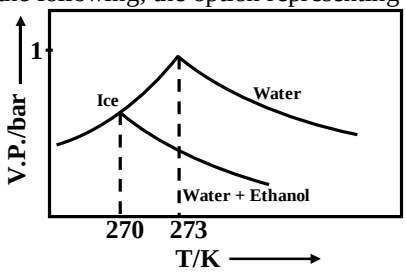
- This section contains **SEVEN** questions
- Each question has **FOUR** options [A], [B], [C] and [D]. **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS
- For each question, marks will be awarded in one of the following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

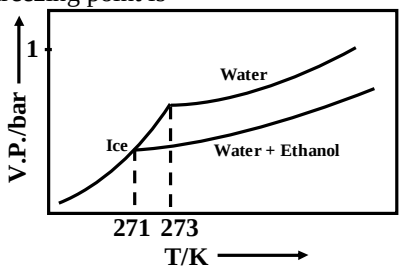
Q.19. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [molecular weight of ethanol is 46 g mol^{-1}]

Among the following, the option representing change the freezing point is

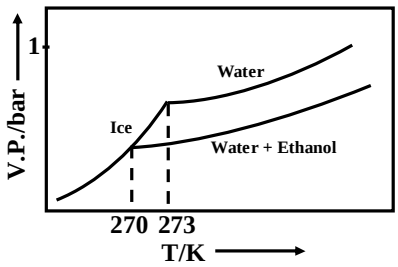
(A)



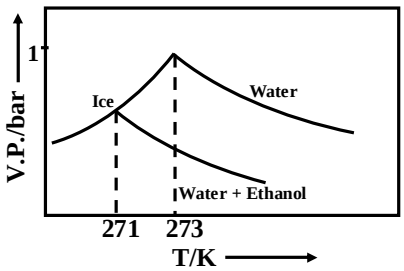
(B)



(C)



(D)



Sol. **C**

$\Delta T_f = K_f \times m$

$= 2 \times \frac{34.5 \times 2}{46}$

$= 2 \times 1.5$

$= 3$

Freezing point of ethanol + water mixture = 273- 3 = 270

Q.20. For the following cell,

$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

When the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is [F is Faraday constant; R is gas constant; T is temperature; $E^0(cell)$ = 1.1 V]

[A] 1.1 F
[B] 2.303 RT – 2.2 F
[C] 2.303 RT + 1.1 F
[D] –2.2 F

Sol. **B**

$Zn - 2e \longrightarrow Zn^{2+}$

$Cu^{2+} + 2e \longrightarrow Cu$

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF}\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$E_{cell} = 1.1 - \frac{2.303RT}{2F}\log 10$$

$$= 1.1 - \frac{2.303RT}{2F}$$

$$\Delta G = -nFE_{cell}$$

$$= -2F\left(1.1 - \frac{2.303RT}{2F}\right)$$

$$= 2.303RT - 2.2\ F$$

*Q.21. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

$$\Delta_f G^0\left[\mathrm{C(graphite)}\right] = 0\ \mathrm{kJmol^{-1}}$$

$$\Delta_f G^0\left[\mathrm{C(diamond)}\right] = 2.9\ \mathrm{kJmol^{-1}}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information: 1 J = 1 kg m^2s^{-2}; 1 Pa = 1 kg $m^{-1}s^{-2}$; 1 bar = 10^5 Pa]

[A] 14501 bar [B] 58001 bar

[C] 1450 bar [D] 29001 bar

Sol. **A**

$$\Delta G = PdV$$

$$\left[\Delta_f G^{o}_{(diamond)} - \Delta_f G^{o}_{(graphite)}\right] = PdV$$

$$2.9\times10^{3}\ \mathrm{J\ mol^{-1}} = P\times2\times10^{-6}\ \mathrm{m^3\ mol^{-1}}$$

$$P = 1.45\times10^{9}\ \mathrm{Pa}$$

$$P = 1.45\times10^{9}\times10^{-5}\ \mathrm{bar}$$

$$P = 1.45 \times 10^4\ \mathrm{bar}$$

$$P = 14500\ \mathrm{bar}$$

Q.22. Which of the following combination will produce H_2 gas?

[A] Fe metal and conc. HNO_3 [B] Cu metal and conc. HNO_3

[C] Zn metal and NaOH(aq) [D] Au metal and NaCN (aq) in the presence of air

Sol. **C**

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$$

*Q.23. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3, and $H_4P_2O_6$ is

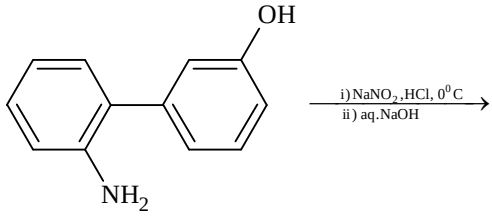
[A] $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$ [B] $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

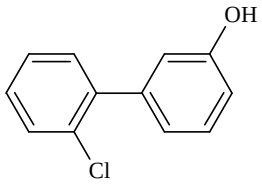
[C] $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$ [D] $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

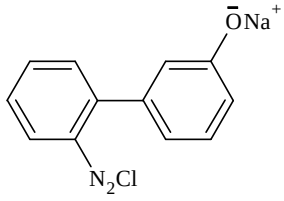
Sol. **C**

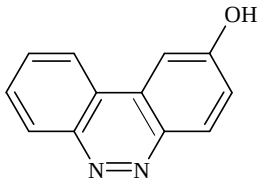
Species	Oxidation state of P
H_3PO_4	+5
$H_4P_2O_6$	+4
H_3PO_3	+3
H_3PO_2	+1

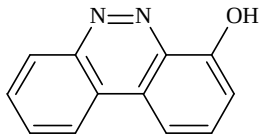
Q.24. The major product of the following reaction is



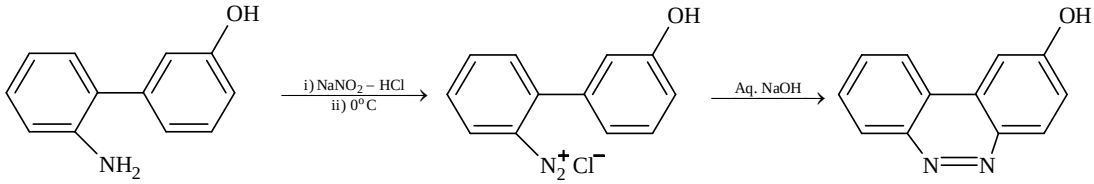
[A] 

[B] 

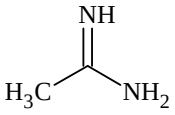
[C] 

[D] 

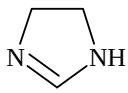
Sol. **C**



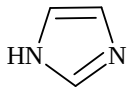
*Q.25. The order of basicity among the following compound is



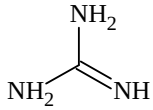
I



II



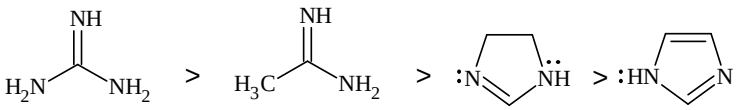
III



IV

[A] II > I > IV > III
[B] IV > II > III > I
[C] IV > I > II > III
[D] I > IV > III > II

Sol. **C**



Conjugate acid has three equivalent canonical forms

Conjugate acid has two equivalent canonical forms

Conjugate acid has two equivalent canonical forms

SECTION 2 [Maximum Marks: 28]

- This section contains **SEVEN** 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 get +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.

Q.26. The correct statement(s) about surface properties is(are)

[A] Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system

[B] The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature

[C] Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium

[D] Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution

Sol. **A, B**

In adsorption process both $\Delta H \& \Delta S$ is – ve. Higher the critical temperature of a gas higher the extent of adsorption.

Cloud is not an emulsion.

Brownian motion depends on the size of the particles.

*Q.27. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant *K* in terms of change in entropy is described by

[A] With increase in temperature, the value of *K* for exothermic reaction decreases because entropy change of the system is positive

[B] With increase in temperature, the value of *K* for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

[C] With increase in temperature, the value of *K* for endothermic reaction increases because the entropy change of the system is negative

[D] With increase in temperature, the value of *K* for exothermic reaction decreases because favourable change in entropy of the surrounding decreases

Sol. **B, D**

[B] With increase in temperature, the value of *K* for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

[D] With increase in temperature, the value of *K* for exothermic reaction decreases because favourable change in entropy of the surrounding decreases

Q.28. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)

[A] The activation energy of the reaction is unaffected by the value of the steric factor

[B] Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

[C] Since P = 4.5, the reaction will not proceed unless an effective catalyst is used

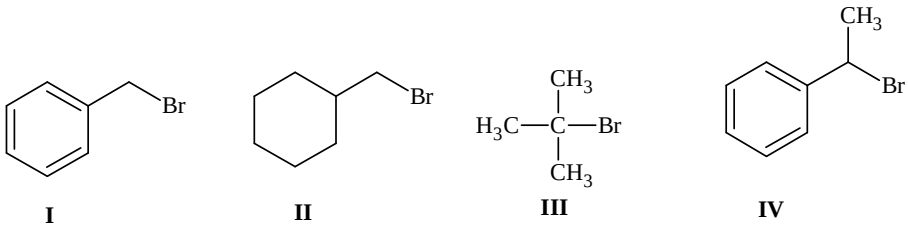
[D] The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

Sol. **A, B**

[A] The activation energy of the reaction is unaffected by the value of the steric factor

[B] Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

Q.29. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is(are)



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

[A] **I** and **III** follow S_N1 mechanism

[B] **I** and **II** follow S_N2 mechanism

[C] Compound **IV** undergoes inversion of configuration

[D] The order of reactivity for **I**, **III** and **IV** is: **IV** > **I** > **III**

Sol. **A, B, C, D**

Benzylic and 3º halides both follow S_N1 mechanism.

Benzylic and 1º halides both follow S_N2 mechanism.

Benzylic 2º halides can undergo inversion of configuration.

The order of reactivity would be IV > I > III if both S_N1 and S_N2 are considered suitably for substrates.

*Q.30. Among the following, the correct statement(s) is(are)

[A] $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure

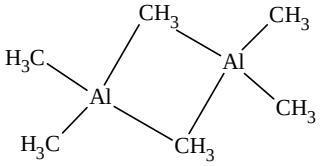
[B] BH_3 has the three-centre two-electron bonds in its dimeric structure

[C] $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure

[D] The Lewis acidity of BCl_3 is greater than that of $AlCl_3$

Sol. **A, B, D**

Both $Al(CH_3)_3$ and BH_3 has 3c – 2e bonds in the dimeric structure.



BCl_3 is stronger Lewis acid than $AlCl_3$.

Q.31. The option(s) with only amphoteric oxides is(are)

[A] Cr_2O_3, BeO, SnO, SnO_2

[B] Cr_2O_3, CrO, SnO, PbO

[C] NO, B_2O_3, PbO, SnO_2

[D] ZnO, Al_2O_3, PbO, PbO_2

Sol. **A, D**

Amphoteric oxides are

ZnO, Al_2O_3, PbO, PbO_2, BeO, SnO, SnO_2, Cr_2O_3

NO is a neutral oxide.

CrO is a basic oxide.

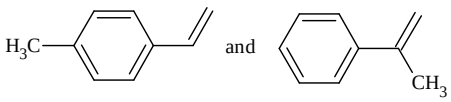
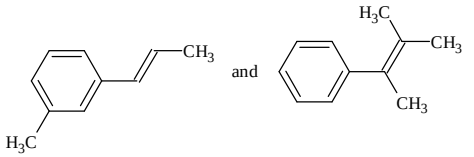
B_2O_3 is an acidic oxide

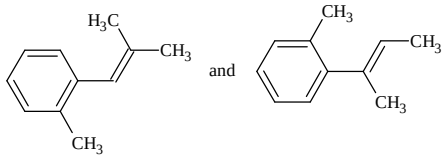
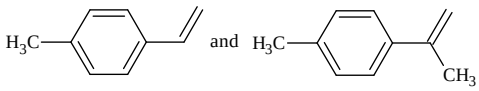
Q.32. Compounds **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is C_8H_8O. **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction.

(i) $\mathbf{P} \xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathbf{Q}}$

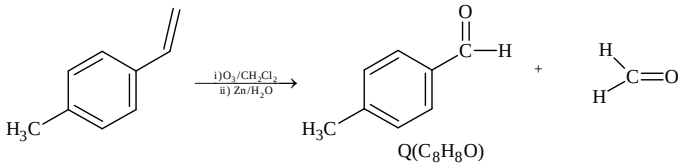
(ii) $\mathbf{R} \xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathbf{S}}$

The option(s) with suitable combination of **P** and **R**, respectively, is(are)

[A]  [B] 

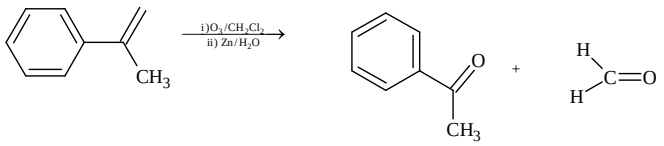
[C]  [D] 

Sol. **A, B**

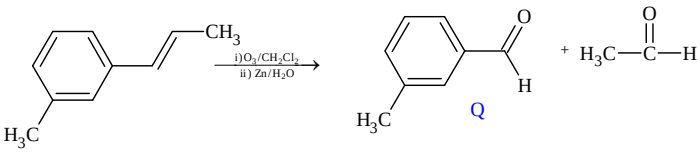


Q(C_8H_8O)

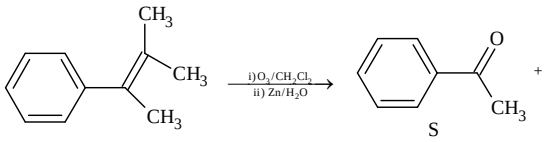
Undergoes Cannizzaro but not haloform



Undergoes Haloform but not Cannizzaro



Undergoes Cannizzaro but not haloform



Undergoes Haloform but not Cannizzaro

For (C) and (D) options no. of carbons are not matching

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

Upon heating $KClO_3$ in the presence of catalytic amount of MnO_2, a gas **W** is formed. Excess amount of **W** reacts with white phosphorus to give **X**. The reaction of **X** with HNO_3 gives **Y** and **Z.**

Q.33 **W** and **X** are, respectively

[A] O_3 and P_4O_6 [B] O_2 and P_4O_6

[C] O_2 and P_4O_{10} [D] O_3 and P_4O_{10}

Q.34 **Y** and **Z** are, respectively

[A] N_2O_3 and H_3PO_4 [B] N_2O_5 and HPO_3

[C] N_2O_4 and HPO_3 [D] N_2O_4 and H_3PO_3

Solution for the Q. No. 33 to 34

$$2KClO_3 \xrightarrow{MnO_2} \underset{W}{2KCl + 3O_2}$$

$$P_4 + 5O_2 \longrightarrow \underset{X}{P_4O_{10}}$$

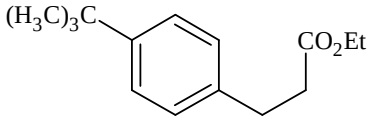
$$P_4O_{10} + 4HNO_3 \longrightarrow 4HPO_3 + 2N_2O_5$$

Q.33. **C**

Q.34. **B**

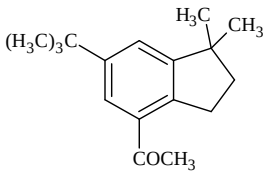
PARAGRAPH 2

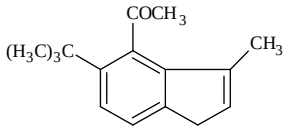
The reaction of compound **P** with CH_3MgBr(excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives **Q.** The compound **Q** on treatment with H_2SO_4 at 0^oC gives **R.** The reaction of **R** with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound **S** [Et in compound **P** is ethyl group]

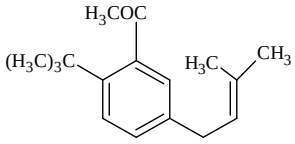


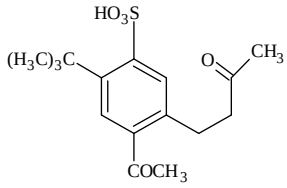
P $\longrightarrow$ **Q** $\longrightarrow$ **R** $\longrightarrow$ **S**

Q. 35 The product **S is**

[A] 

[B] 

[C] 

[D] 

*Q. 36 The reactions, **Q** to **R** and **R** to **S**, are

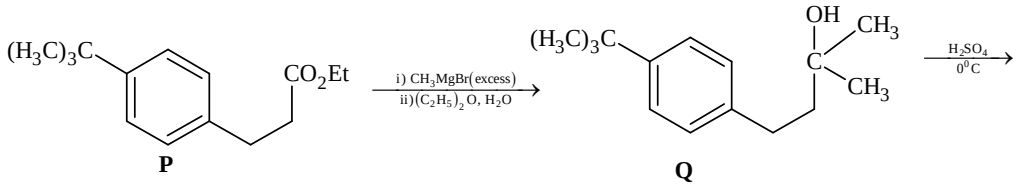
[A] Dehydration and Friedel-Crafts acylation

[B] Aromatic sulfonation and Friedel-Crafts acylation

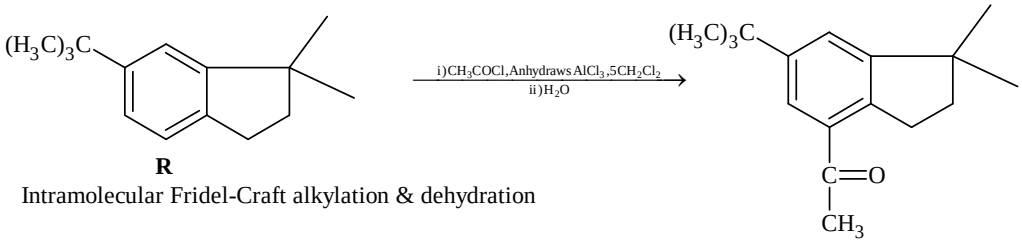
[C] Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation

[D] Friedel-Crafts alkylation and Friedel-Crafts acylation

Solution for the Q. No. 35 to 36



P **Q**



R

Intramolecular Fridel-Craft alkylation & dehydration

Fridel-Craft alkylation

Q.35. **A**

Q.36. **C**