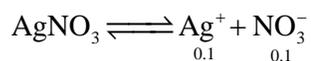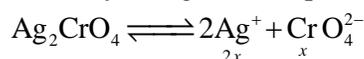# PART (B) : CHEMISTRY

SECTION-I : (SINGLE ANSWER CORRECT TYPE)

This section contains **04 multiple choice questions.** Each question has four choices (A), (B), (C) and (D) out of which **ONLY ONE is correct.**

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21. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in 0.1 M $AgNO_3$ solution is 1.1×10^{-P}. The value of P is

(A) 11   (B) 10   (C) 12   (D) 9

21. **(B)**

In presence of common ion (in this case Ag^+ ion), solubility of sparingly soluble salt is decreased.

Let, solubility of Ag_2CrO_4 in presence of 0.1 M $AgNO_3 = x$

$$Ag_2CrO_4 \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

$$AgNO_3 \rightleftharpoons \underset{0.1}{Ag^+} + \underset{0.1}{NO_3^-}$$

Total $[Ag^+] = (2x + 0.1)M \approx 0.1 M$

As, $x <<< 0.1 M$

$$\left[CrO_4^{2-}\right] = xM$$

Thus, $\left[Ag^+\right]^2 \left[CrO_4^{2-}\right] = K_{sp}$

$$(0.1)^2(x) = 1.1 \times 10^{-12}$$

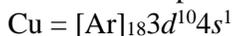$\therefore \quad x = 1.1 \times 10^{-10} M$

22. Which of the following statements is correct?

(A) Hydrated $FeCl_3$ forms anhy. $FeCl_3$ on heating

(B) Solution of Hg_2Cl_2 turns black, when NH_3 is added in it

(C) Aqueous solutions of $HgCl_2$ and $SnCl_2$ can co-exist

(D) CuCl is soluble in water while $CuCl_2$ is insoluble

22. **(B)**

(A) Hydrated $FeCl_3$ does not form anhyd. $FeCl_3$, on heating because it forms Fe_2O_3.

$$2FeCl_3 \cdot 6H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl + 9H_2O$$

(B) Solution of Hg_2Cl_2 turns black, when NH_3 is added in it this is due to formation of $HgNH_2Cl$ & Hg.

(C) Aqueous solution of $HgCl_2$ and $SnCl_2$ cannot co-exist because $SnCl_2$ reduces $HgCl_2$ to Hg.

(D) CuCl is insoluble in water while $CuCl_2$ is soluble.

23. Which pair of compounds is expected to show similar colour in aqueous medium?

(A) $FeCl_2$ and $CuCl_2$ (B) $VOCl_2$ and $CuCl_2$

(C) $VOCl_2$ and $FeCl_2$ (D) $FeCl_2$ and $MnCl_2$

23. **(B)**

Colour of transition metal ion salt is due to d-d transition of unpaired electrons of d-orbital. Metal ion salt having similar number of unpaired electrons in d-orbitals shows similar colour in aqueous medium. In $VOCl_2$, vanadium is present as V^{4+} and in $CuCl_2$, copper is present as Cu^{2+}

$$V = [Ar]_{18} 3d^3 4s^2$$

$V^{4+} = [Ar]_{18}3d^1$

∴ Number of unpaired electron = 1

$Cu = [Ar]_{18}3d^{10}4s^1$

$Cu^{2+} = [Ar]_{18}3d^9$

∴ Number of unpaired electron = 1

Hence, $VOCl_2$ and $CuCl_2$ show similar colour.

24. In the reaction, $P + Q \rightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies as exponential decay with reaction time as shown in the figure. The overall order of the reaction is
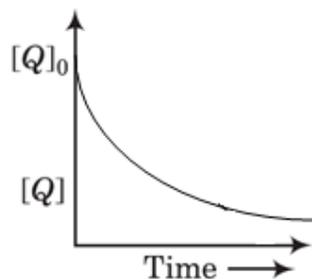
(A) 3   (B) 2   (C) 1   (D) 1

24. **(B)**

Time for 75% reaction is twice the time taken for 50% reaction if it is first order reaction wrt P.

From graph, $[Q]$ decreases exponentialy with time, thus it is first order reaction wrt Q.

$$\frac{dx}{dt} = K[P]^a[Q]^b$$

Order wrt $P = a = 1$

Order wrt $Q = b = 1$

Thus, overall order of the reaction = 1 + 1 = 2.

SECTION-II : (COMPREHENSIONS TYPE)

This section contains **06** questions. Based on each paragraph, there are **TWO** questions. Each question has 4 choices (A), (B), (C) and (D) for its answer, out which **ONLY ONE** is correct.

PARAGRAPH FOR QUESTIONS NO. 25 & 26

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is constant (– 57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

25. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt.2 is

(A) 1.0   (B) 10.0   (C) 24.5   (D) 51.4

25. **(A)**

Since, enthalpy of neutralisation of a strong acid with a strong base is constant and equal to – 57.0 kJ mol^{-1}. Hence, for calculating the value of enthalpy of dissociation for acetic acid, we need to

calculate enthalpy of neutralisation of CH_3COOH first. After this we can easily find enthalpy of dissociation of CH_3COOH as

Enthalpy of a dissociation of CH_3COOH = enthalpy of neutralisation of a strong acid (HCl) with strong base, (NaOH) – enthalpy of neutralisation of CH_3COOH with strong base (NaOH).

Let the heat capacity of insulated beaker is C. Mass of aqueous content in Expt.1

$$= (100 + 100) \times 1 = 200 \text{ g}$$

Total heat capacity $= (C + 200 \times 4.2) \text{ J/K}$

Also, mole of acid-base neutralised in Expt.1

$$= 0.1 \times 1 = 0.1$$

Hat released in Exp.1

$$= 0.1 \times 57 = 5.7 \text{ kJ}$$

$$5.7 \times 1000 = (C + 200 \times 4.2) \Delta T$$

$$5.7 \times 1000 = (C + 200 \times 4.2) \times 5.7$$

$$C + 200 \times 4.2 = 1000$$

In 2nd Exp. $n_{CH_3COOH} = 0.2, n_{NaOH} = 0.1$

Total mass of aqueous content = 200 g

$\Rightarrow$ Total heat capacity $(C + 200 \times 4.2) = 1000$

Heat released $= 1000 \times 5.6 = 5600 \text{ J}$

Overall only 0.1 mole of CH_3COOH taking part in neutralisation,

$\Rightarrow \quad \Delta H_{neutralisation}$ of $CH_3COOH = -\dfrac{5600}{0.1} = -56000 \text{ J/mol}$

$\Rightarrow \quad \Delta H_{ionisation}$ of $CH_3COOH = 57 - 56 = 1 \text{ kJ/mol}$

26.   The pH of the solution after Expt.2 is

(A) 2.8   (B) 4.7   (C) 5.0   (D) 7.0

26.   **(B)**

Out of 0.2 mole of CH_3COOH only 0.1 mole of CH_3COOH are taking part in the neutralisation reaction with NaOH. In the final solution, 0.1 mole of CH_3COOH and 0.1 mole of $CH_3COOHNa$ is a salt and dissociates almost completely and reverse the reaction till equilibrium is reached.

Hence, final solution is a buffer solution and we may use following formula to calculate its pH as

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Acording to the formula of pH relating to pK_a

$$pH = pK_a + \log \frac{\left[CH_3COO^- \right]}{[CH_3COOH]}$$

$$pH = -\log [K_a] + \log \frac{\left[CH_3COO^- \right]}{[CH_3COOH]}$$

$$pH = -\log (2 \times 10^{-5}) + \log \frac{0.1}{0.1}$$

$$pH = 5 - \log 2 + 0 = 4.7$$
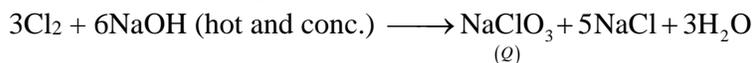
PARAGRAPH FOR QUESTIONS NO. 27 & 28

The reactions of Cl_2 gas with cold dilute and hot conc. NaOH in water give sodium salts of two (different) oxoacids of chlorine, *P* and *Q*, respectively. The reaction of F_2 with cold dil. NaOH and hot conc. NaOH gives gases R and S respectively.

27. *P* and *Q* respectively are the sodium salts of
    (A) hypochlorous and chloric acids   (B) hypochlorous and chlorous acids
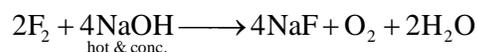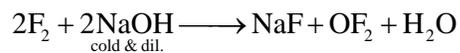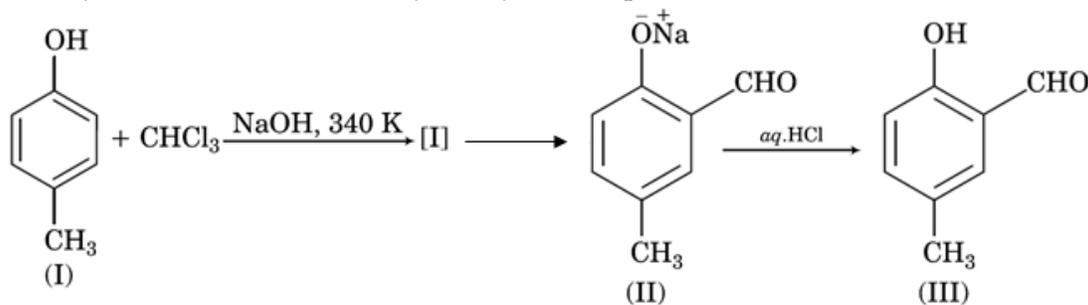   (C) chloric and perchloric acids   (D) chloric and hypochlorous acids

27. **(A)**

$$Cl_2 + 2NaOH \text{ (cold and dil.)} \longrightarrow \underset{(P)}{NaOCl} + NaCl + H_2O$$
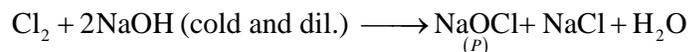
NaOCl is sodium hypochlorite

$$3Cl_2 + 6NaOH \text{ (hot and conc.)} \longrightarrow \underset{(Q)}{NaClO_3} + 5NaCl + 3H_2O$$

28. R and S respectively are
    (A) OF_2 and O_2 (B) HF and O_2F_2 (C) O_2 and O_2F_2 (D) O_2 and HF

28. **(A)**

$$2F_2 + \underset{\text{cold \& dil.}}{2NaOH} \longrightarrow NaF + OF_2 + H_2O$$

$$2F_2 + \underset{\text{hot \& conc.}}{4NaOH} \longrightarrow 4NaF + O_2 + 2H_2O$$
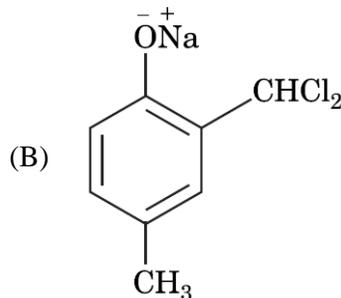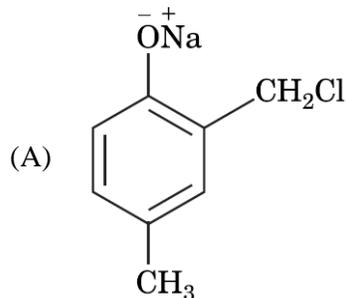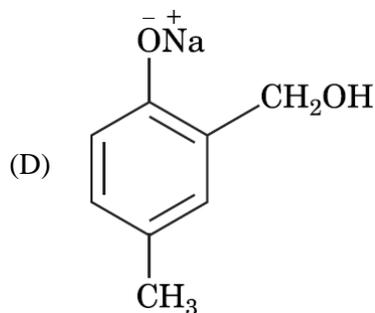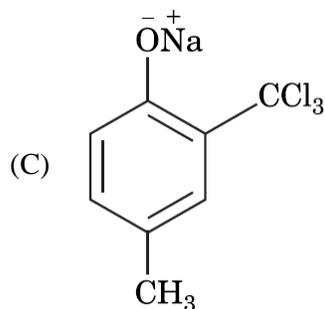
PARAGRAPH FOR QUESTIONS NO. 29 & 30

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involes electrophilic aromatic substitution. This is general method for the synthesis of substituted salicylaldehydes as depicted below.
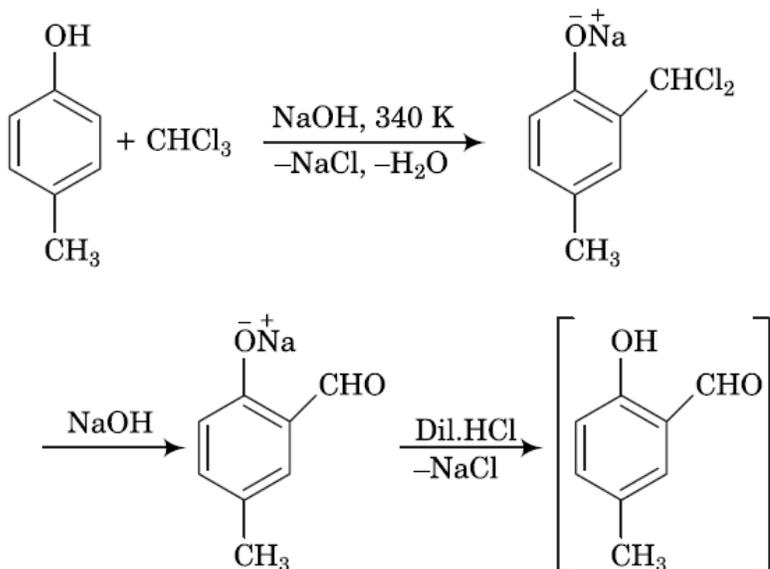

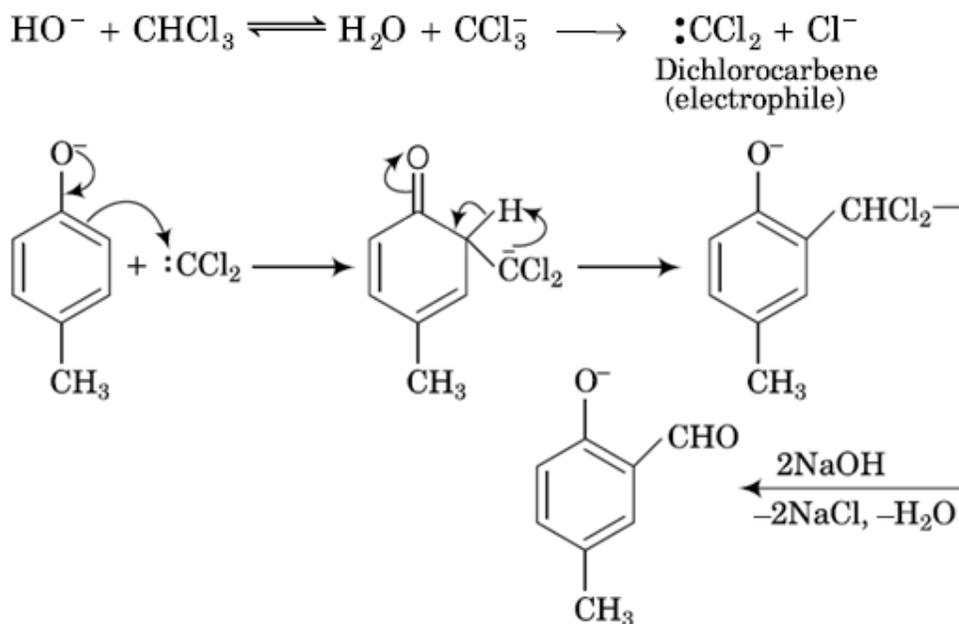29. The structure of the intermediate [I] is

(C) [structure: sodium phenolate with CCl_3 ortho and CH_3 para]

(D) [structure: sodium phenolate with CH_2OH ortho and CH_3 para]

29.   **(B)**

[structure: p-cresol (OH with CH₃ para) + CHCl₃ →(NaOH, 340 K; –NaCl, –H₂O)→ sodium phenolate with CHCl₂ ortho, CH₃ para]

[→(NaOH)→ sodium phenolate with CHO ortho, CH₃ para →(Dil.HCl; –NaCl)→ [2-hydroxy-5-methylbenzaldehyde (OH, CHO ortho, CH₃ para)]]

30.   The electrophile in the reaction is

(A) $:CHCl$ (B) $\overset{+}{C}HCl_2$ (C) $:CCl_2$ (D) $\cdot CCl_3$

30.   **(C)**

$$HO^- + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \longrightarrow :CCl_2 + Cl^-$$
Dichlorocarbene
(electrophile)

[mechanism: phenolate + :CCl₂ → intermediate with CCl₂ and H → CHCl₂ phenolate → (2NaOH; –2NaCl, –H₂O) → CHO phenolate]

SECTION-III : (MULTIPLE CORRECT ANSWER(S) TYPE)

This section contains **06 multiple choice questions.** Each question has four choices (A), (B), (C) and (D) out of which **ONE or MORE than one is/are correct.**

---

31. $H - \overset{\overset{O}{||}}{C} - OH$ and $CH_3 - \overset{\overset{O}{||}}{C} - OH$ can be distinguished by

(A) $NaHCO_3$ (B) H_2SO_4 (C) $AgNO_3 / NH_4OH$ (D) Fehlings solution

31.   (CD)

32. Which of the followign statements are correct?
(A) In the extraction of Ag from $[Ag(CN)_2]^-$, Zn is used
(B) When, NH_4OH is added to copper sulphate solution, a deep blue colour appears
(C) $AgNO_3$ is called lunar caustic
(D) $AgNO_3$ gives white precipitate with NaCl but not with CCl_4

32.   (ABCD)
(A) Zn is stronger reducing agent than Cu and cheaper than Cu also.

$$Zn + 2\left[Ag\left(CN\right)_2\right]^- \longrightarrow \left[Zn\left(CN\right)_4\right]^- + 2Ag$$

(B) Due to the formaiton of blue copper tetraammine sulphate, $[Cu(NH_3)_4]SO_4$ complex.
(C) When bought in contact with skin, it leans black stain as present on moon.
(D) NaCl is ionic compound and Cl^- ions obtained from it reacts with Ag^+ to form white AgCl. CCl_4 is covalent compound so it does not give Cl^- and hence, white precipate of AlCl.
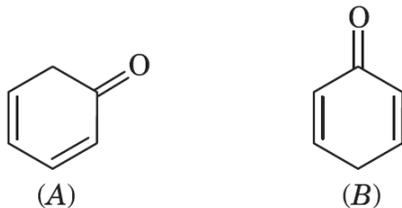
33. Which of the following will give yellow precipitate with $I_2/NaOH$?
(A) $I - CH_2 - CO - CH_2 - CH_3$ (B) $CH_3 - COOCOCH_3$
(C) $H_3C - CO - NH_2$ (D) $CH_3 - CH(OH)CH_2CH_3$

33.   (AD)
Conceptual

34. Consider the following two structures *A* and *B*

   *(A)*   *(B)*

and choose the correct options.
(A) *A* is more stable than *B*
(B) Both *A* and *B* shows keto-enol tautomerism
(C) *A* has acidic hydrogen whereas *B* has not
(D) The enol-form of *A* and *B* are more stable than keto-form

34.   (ABD)

(A)   (B)
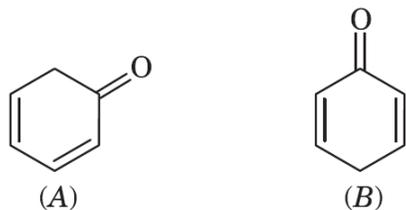
Due to the presence of α-hydrogen, they shows tautomerism, i.e. shows keto-enol tautomerism.
Enol form of both A and B have an aromating ring.
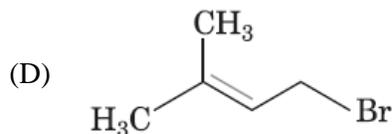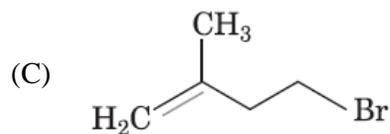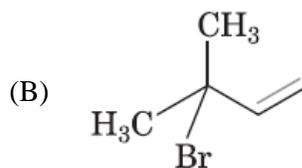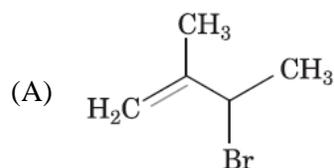So, they are more stable than their respective keto-forms.

Keto-form   Enol-form
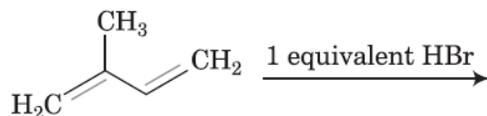

Keto-form   Enol-form
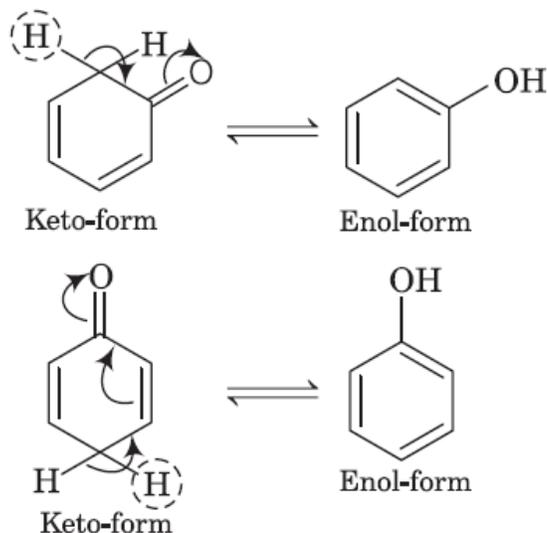
35. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?

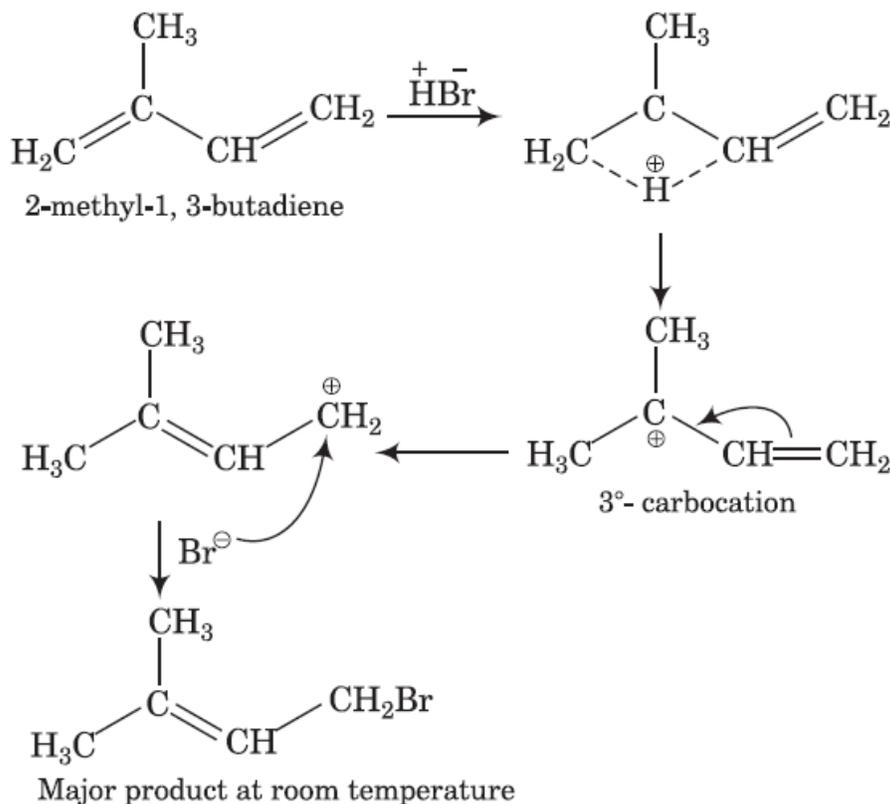(A) $CaSO_4$ (B) $BeSO_4$ (C) $BaSO_4$ (D) $SrSO_4$

35. **(B)**

36. In the followign reaction, the major product is

(A)   (B)

(C)   (D)

36. **(D)**

When 2-methyl-1,3 butadiene reacts with 1 equivalent of HBr, it undergoes Markownikoff's addition forming a π-bond lesser compound than the stading compound.
Reaction looks like,

2-methyl-1, 3-butadiene

3°- carbocation

Major product at room temperature

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SECTION-IV : (INTEGER ANSWER TYPE)

This section contains **04** questions. The answer to each question is a **NUMERICAL VALUE.** For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, 0.33, 30.27, 127.30)

37. A 0.001 molal solution of $[Pt(NH_3)_4Cl_n]Cl_{4-n}$ in water had a freezing point depression of 0.0054°C. Assuming 100% ionisation of the complex. Find the value of $n[K_f(H_2O) = 1.8$ K-Kg / mol].

37. **(2)**

In the given complex, there are four NH_3 (which are the ligands only) and four Cl (which can be either ligands or ionisable ions or both). If there are nCl ligands then ionisable Cl ligands will be (4 – n). Knowing van't Hoff factor (i) for $[Pt(NH_3)_4Cl_n]Cl_{4-n}$, n can be calculated.

$$\left[Pt\left(NH_3\right)_4 Cl_n\right]Cl_{4-n} = \left[Pt\left(NH_3\right)_4 Cl_n\right]^{(4-n)} + \left(4-n\right)Cl^-$$
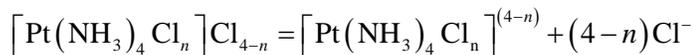
Total number of ions after dissociation,

$$n' = \left(4-n\right)+1 = 5-n$$

Hence, van't Hoff factor

$$i = 1+\left(n'-1\right)\alpha = 1+\left(5-n-1\right)1 = 5-n$$

Where, n' = number of ions from one mole complex.

$$\Delta T_f = K_f mi$$

$$0.0054 = 1.86 \times 0.001\left(5-n\right)$$

$n = 2.1 \simeq 2$ (n is whole number)

Hence, complex is $[Pt(NH_3)_4Cl_2]Cl_2$

38. 50cc of 0.04 M $K_2Cr_2O_7$ in acidic medium oxidizes a sample of H_2S gas to sulphur. Volume of 0.03 M $KMnO_4$ required to oxidize the same amount of H_2S gas to sulphur in acidic medium is $10 \times x$ mL. The value of x is

38. **(8)**

Milliequivalents of $K_2Cr_2O_7$ reacted with $H_2S(N_1V_1)$ = milliequivalent of $KMnO_4$ reacted with H_2S (N_2V_2)
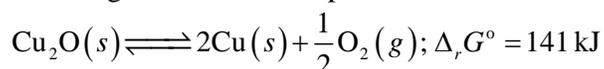
i.e. miliequivalent of $KMnO_4$ = milliequivalent of H_2S.

Therefore, $50 \times 0.04 \times 6 = V_2 \times 0.03 \times 5$

$\quad V_2 = 80\,mL$

$\therefore$ The value of $x = 8$

39. The following reaction is non-spontaneous at 25°C,

$$Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g); \Delta_r G° = 141\,kJ$$

If $\Delta_r S° = 75.18\ JK^{-1}$ and at temperature above $(2170 + x)K$, the reaction becomes spontaneous.

Calculate the value of x. (Assume $\Delta_r H°$ and $\Delta_r S°$ do not vary with temperature)

39. **(6)**

At $T = 25°C = 298K$, we have

$\quad \Delta G = \Delta H - T\Delta S$

$\quad 141 = \Delta H - 298 \times 0.0758$

$\quad \Delta H = 141 + 298 \times 0.0758 = 163.6\,kJ$

The temperature above which the reaction becomes spontaneous under standard conditions corresponds to $\Delta G = 0$ and is given by

$$T = \frac{\Delta H}{\Delta S}$$

Substituting the value of ΔH and ΔS, it gives

$$T = \frac{163.6 \times 10^3\,J}{75.18\ JK^{-1}} = 2176\,K$$
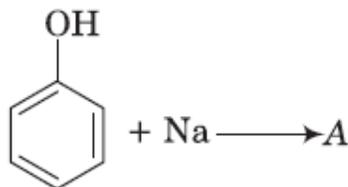
Above, 2176 K, the reaction will become spontaneous.
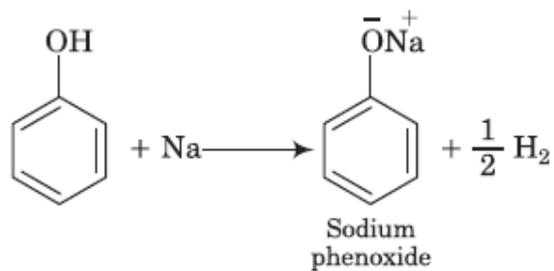
As $T = 2176$ K

So, $T = (2170 + 6)$ K

Hence, $x = 6$

40. The number of resonance structure(s) for A is

40. **(5)**

Phenoxide ion undergoes resonance and get stabilised.