JEE ADVANCED (Paper - 2)

CHEMISTRY

Code - 4

SECTION 1 (Maximum Marks: 32)

- This section contains **EIGHT** questions
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive
- For each question, darken the bubble corresponding to the correct integer in the ORS
- Marking scheme:
 - +4 If the bubble corresponding to the answer is darkened
 - 0 In all other cases
- *21. In dilute aqueous H₂SO₄, the complex diaquodioxalatoferrate(II) is oxidized by MnO₄⁻. For this reaction, the ratio of the rate of change of [H⁺] to the rate of change of [MnO₄⁻] is
- *22. The number of hydroxyl group(s) in **Q** is

23. Among the following, the number of reaction(s) that produce(s) benzaldehyde is

$$I \qquad \qquad \begin{array}{c} \text{CO, HCI} \\ \hline Anhydrous \text{AlCl}_3/\text{CuCl} \end{array}$$

$$II \qquad \begin{array}{c} \text{CHCl}_2 \\ \hline \\ \hline \\ H_2O \\ \hline \\ 100^{\circ}\text{C} \end{array}$$

$$COCl \qquad \qquad \begin{array}{c} \text{H}_2 \\ \hline \\ Pd-BaSO_4 \end{array}$$

$$CO_2Me \qquad \qquad \begin{array}{c} \text{DIBAL-H} \\ \hline \\ \\ H_2O \end{array}$$

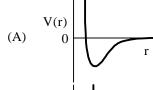
- 24. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is
- 25. Among the complex ions, $[Co(NH_2-CH_2-NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2-CH_2-NH_2)_2(NH_3)Cl_3]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl_3]^{2+}$, the number of complex ion(s) that show(s) cis-trans isomerism is
- *26. Three moles of B₂H₆ are completely reacted with methanol. The number of moles of boron containing product formed is
- 27. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda_{X^-}^0 \approx \lambda_{Y^-}^0$, the difference in their pK_a values, pK_a(HX)-pK_a(HY), is (consider degree of ionization of both acids to be << 1)

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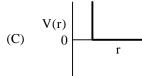
28. A closed vessel with rigid walls contains 1 mol of $^{238}_{92}$ U and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}$ U to $^{206}_{82}$ Pb, the ratio of the final pressure to the initial pressure of the system at 298 K is

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
- Marking scheme:
 - +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened
 - 0 If none of the bubbles is darkened
 - -2 In all other cases
- *29. One mole of a monoatomic real gas satisfies the equation p(V b) = RT where b is a constant. The relationship of interatomic potential V(r) and interatomic distance r for the gas is given by



(B) V(r) r



(D) V(r) r

30. In the following reactions, the product S is

$$\begin{array}{c} H_3C \\ \hline \\ ii.Zn,H_2O \\ \end{array} \rightarrow \mathbf{R} \xrightarrow{NH_3} S$$

$$(A) \qquad \qquad H_3C \qquad \qquad N$$

31. The major product **U** in the following reactions is

$$(B) \qquad \begin{array}{c} H_3C & CH_3 \\ O & O \end{array}$$

$$(D) \qquad \begin{array}{c} CH_2 \\ O \\ O \end{array} \qquad H$$

32. In the following reactions, the major product W is

$$NH_2 \xrightarrow{\text{NaNO}_2, \text{HCl}} \mathbf{V} \xrightarrow{\text{OH}} \mathbf{W}$$

$$(A) \qquad N = N \qquad OH$$

*33. The correct statement(s) regarding, (i) HClO, (ii) HClO₂, (iii) HClO₃ and (iv) HClO₄, is (are)

(D)

- (A) The number of Cl = O bonds in (ii) and (iii) together is two
- (B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
- (C) The hybridization of Cl in (iv) is sp³
- (D) Amongst (i) to (iv), the strongest acid is (i)

- 34. The pair(s) of ions where BOTH the ions are precipitated upon passing H₂S gas in presence of dilute HCl, is(are)
 - (A) Ba²⁺, Zn²⁺ (C) Cu²⁺, Pb²⁺

(B) Bi³⁺, Fe³⁺ (D) Hg²⁺, Bi³⁺

- *35. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
 - (A) CH₃SiCl₃ and Si(CH₃)₄

(B) (CH₃)₂SiCl₂ and (CH₃)₃SiCl

(C) (CH₃)₂SiCl₂ and CH₃SiCl₃

- (D) SiCl₄ and (CH₃)₃SiCl
- When O2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O2. The TRUE 36. statement(s) regarding this adsorption is(are)
 - (A) O₂ is physisorbed

- (B) heat is released
- (C) occupancy of π_{2p}^* of O_2 is increased
- (D) bond length of O₂ is increased

SECTION 3 (Maximum Marks: 16)

- This section contains TWO paragraphs
- Based on each paragraph, there will be TWO 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
- Marking scheme:
 - +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened
 - 0 In none of the bubbles is darkened
 - −2 In all other cases

PARAGRAPH 1

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 neutralization of a strong acid with a strong base is a 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

(Consider heat capacity of all solutions as 4.2 J g⁻¹ K⁻¹ and density of all solutions as 1.0 g mL⁻¹)

- Enthalpy of dissociation (in kJ mol⁻¹) of acetic acid obtained from the **Expt. 2** is *37.
 - (A) 1.0

(B) 10.0

(C) 24.5

(D) 51.4

*38. The pH of the solution after Expt. 2 is

(A) 2.8

(B) 4.7

(C) 5.0

(D) 7.0

PARAGRAPH 2

In the following reactions
$$C_8H_6 \xrightarrow{Pd\text{-BaSO}_4} C_8H_8 \xrightarrow{i.B_2H_6} X$$

$$\downarrow^{H_2O}_{HgSO_4, H_2SO_4}$$

$$C_8H_8O \xrightarrow{i.EtMgBr, H_2O} Y$$

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39. Compound **X** is

40. The major compound \mathbf{Y} is

$$(A) \hspace{1cm} CH_3$$

$$(C) \qquad \begin{array}{c} CH_2 \\ CH_3 \end{array}$$

$$(B) \qquad \begin{array}{c} OH \\ CH_3 \end{array}$$

$$(B) \hspace{1cm} CH_3$$

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21.	8	22.	4	23.	4	24.	3
25.	5	26.	6	27.	3	28.	9
29.	\mathbf{C}	30.	\mathbf{A}	31.	В	32.	\mathbf{A}
33.	B, C	34.	C, D	35.	В	36.	B,C,D
37	A	38	R	39	C	40	D ,

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SOLUTIONS

CHEMISTRY

21. $\left[\operatorname{Fe}(\operatorname{C}_2\operatorname{O}_4)(\operatorname{H}_2\operatorname{O})\right]^{2^-} + \operatorname{MnO}_4^{2^-} + 8\operatorname{H}^+ \longrightarrow \operatorname{Mn}^{2^+} + \operatorname{Fe}^{3^+} + 4\operatorname{CO}_2 + 6\operatorname{H}_2\operatorname{O}$ So the ratio of rate of change of $[\operatorname{H}^+]$ to that of rate of change of $[\operatorname{MnO}_4^-]$ is 8.

22.
$$\begin{array}{c} H \\ HO \end{array}$$

$$\begin{array}{c} H^{+} \\ A \end{array}$$

$$\begin{array}{c} (P) \\ \text{aqueous dilute KMnO}_{4} \text{ (excess)} \\ 0^{0}C \\ \text{OH} \\ \text{HO} \end{array}$$

$$\begin{array}{c} OH \\ OH \\ (Q) \end{array}$$

24.
$$Et_{3}P \downarrow C CH_{3}$$

$$OC \downarrow Br$$

The number of Fe - C bonds is 3.

25. $\left[\text{Co(en)}_2 \text{Cl}_2 \right]^+ \longrightarrow \text{will show cis-trans isomerism}$ $\left[\text{CrCl}_2 \left(\text{C}_2 \text{O}_4 \right)_2 \right]^{3^-} \longrightarrow \text{will show cis-trans isomerism}$ $\left[\text{Fe} \left(\text{H}_2 \text{O} \right)_4 \left(\text{OH} \right)_2 \right]^+ \longrightarrow \text{will show cis-trans isomerism}$ $\left[\text{Fe} \left(\text{CN} \right)_4 \left(\text{NH}_3 \right)_2 \right]^- \longrightarrow \text{will show cis-trans isomerism}$ $\left[\text{Co(en)}_2 \left(\text{NH}_3 \right) \text{Cl} \right]^{2^+} \longrightarrow \text{will show cis-trans isomerism}$ $\left[\text{Co(NH}_3)_4 \left(\text{H}_2 \text{O} \right) \text{Cl} \right]^{2^+} \longrightarrow \text{will not show cis-trans isomerism (Although it will show geometrical isomerism)}$

- 26. B₂H₆ + 6MeOH → 2B(OMe)₃ + 6H₂
 1 mole of B₂H₆ reacts with 6 mole of MeOH to give 2 moles of B(OMe)₃.
 3 mole of B₂H₆ will react with 18 mole of MeOH to give 6 moles of B(OMe)₃
- 27. $HX \rightleftharpoons H^{+} + X^{-}$ $Ka = \frac{\left[H^{+}\right]\left[X^{-}\right]}{\left[HX\right]}$ $HY \rightleftharpoons H^{+} + Y^{-}$ $Ka = \frac{\left[H^{+}\right]\left[Y^{-}\right]}{\left[HY\right]}$ $\Lambda_{m} \text{ for } HX = \Lambda_{m_{1}}$ $\Lambda_{m} \text{ for } HY = \Lambda_{m_{2}}$ $\Lambda_{m_{1}} = \frac{1}{10}\Lambda_{m_{2}}$ $Ka = C\alpha^{2}$ $Ka_{1} = C_{1} \times \left(\frac{\Lambda_{m_{1}}}{\Lambda_{m_{1}}^{0}}\right)^{2}$

$$\begin{split} Ka_{2} &= C_{2} \times \left(\frac{\Lambda_{m_{2}}}{\Lambda_{m_{2}}^{0}}\right)^{2} \\ &\frac{Ka_{1}}{Ka_{2}} = \frac{C_{1}}{C_{2}} \times \left(\frac{\Lambda_{m_{1}}}{\Lambda_{m_{2}}}\right)^{2} = \frac{0.01}{0.1} \times \left(\frac{1}{10}\right)^{2} = 0.001 \\ pKa_{1} - pKa_{2} = 3 \end{split}$$

- 28. In conversion of ${}^{238}_{92}$ U to ${}^{206}_{82}$ Pb , 8α particles and 6β particles are ejected. The number of gaseous moles initially = 1 mol The number of gaseous moles finally = 1 + 8 mol; (1 mol from air and 8 mol of ${}_{2}$ He 4) So the ratio = 9/1 = 9
- 29. At large inter-ionic distances (because $a \to 0$) the P.E. would remain constant. However, when $r \to 0$; repulsion would suddenly increase.

30.
$$H_{3}C$$

31.
$$+ H_3C - CH - CH_3 \longrightarrow CH_3$$

$$+ H_3C - CH - CH_3 \longrightarrow CH_3$$

$$+ H_3C - CH_3 \longrightarrow CH_3$$

$$+ H_3C - CH_3 \longrightarrow CH_3 \longrightarrow CH_3$$

$$+ H_3C - CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3$$

$$+ H_3C - CH_3 \longrightarrow CH_3$$

32.
$$\begin{array}{c}
N = N - Ph \\
N_2 & Cl \\
\hline
N_2 & N = N - Ph \\
N_2 & N = N - Ph \\
N_2 & N = N - Ph \\
N_3 & N = N - Ph \\
N_4 & N = N - Ph \\
N_5 & N = N - Ph \\
N_6 & N = N - Ph \\
N_7 & N = N - Ph \\
N_8 & N = N - Ph \\
N_8 & N = N - Ph \\
N_8 & N = N - Ph \\
N_9 & N = N -$$

34. Cu²⁺, Pb²⁺, Hg²⁺, Bi³⁺ give ppt with H₂S in presence of dilute HCl.

35.
$$\begin{array}{c} CH_3 & CH_3 \\ CI-Si-Cl \xrightarrow{H_2O} HO \xrightarrow{Si-OH} \xrightarrow{H-O} H-O \xrightarrow{Si-O-Si} O-H \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} CH_3 & CH_3 \\ Si-O-Si \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ Si-O-Si \\ Si-O-Si \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ CH_3 & CH_3 \end{array}$$

$$\begin{array}{c} Me \\ Me \\ CH_3 & CH_3 \end{array}$$

36. * Adsorption of O₂ on metal surface is exothermic.

* During electron transfer from metal to O_2 electron occupies π^*_{2p} orbital of O_2 .

* Due to electron transfer to O₂ the bond order of O₂ decreases hence bond length increases.

37.
$$HCl + NaOH \longrightarrow NaCl + H_2O$$

 $n = 100 \times 1 = 100 \text{ m mole} = 0.1 \text{ mole}$

Energy evolved due to neutralization of HCl and NaOH = $0.1 \times 57 = 5.7$ kJ = 5700 Joule Energy used to increase temperature of solution = $200 \times 4.2 \times 5.7 = 4788$ Joule

Energy used to increase temperature of calorimeter = 5700 - 4788 = 912 Joule

 $ms.\Delta t = 912$

 $m.s \times 5.7 = 912$

ms = 160 Joule/°C [Calorimeter constant]

Energy evolved by neutralization of CH₃COOH and NaOH

 $= 200 \times 4.2 \times 5.6 + 160 \times 5.6 = 5600$ Joule

So energy used in dissociation of 0.1 mole $CH_3COOH = 5700 - 5600 = 100$ Joule Enthalpy of dissociation = 1 kJ/mole

38.
$$CH_3COOH = \frac{1 \times 100}{200} = \frac{1}{2}$$

$$CH_3CONa = \frac{1 \times 100}{200} = \frac{1}{2}$$

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

$$pH = 5 - \log 2 + \log \frac{1/2}{1/2}$$

$$pH = 4.7$$

39.
$$C_8H_6 \longrightarrow = \text{double bond equivalent} = 8 + 1 - \frac{6}{2} = 6$$

$$\frac{\text{Pd/BaSO}_4}{\text{H}_2}$$

$$\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$$

$$\begin{array}{c} \text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O} \\ \text{O} \\ \text{||} \\ \text{C--CH}_3 \end{array}$$

(i) EtMgBr (ii) H₂O

$$\begin{array}{ccc}
& & \downarrow & & & \downarrow \\
& & OH & & & CH_3 \\
& & \downarrow & & & \downarrow \\
Ph & & & C & & CH_3 & & H^+/heat \\
& & & & & & & & & & & & & & \\
\end{array}$$