JEE(ADVANCED) 2013
## Paper - 1 [Code - 5]

CHEMISTRY

SECTION – 1
(Only One option correct Type)

This section contains **10 multiple choice questions.** Each question has four choices (A), (B), (C) and (D) out of which **ONLY ONE** is correct.

*21. In the reaction,

$$P + Q \longrightarrow R + S$$

the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is
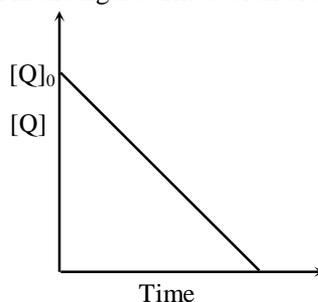
(A) 2   (B) 3
(C) 0   (D) 1

Sol. **(D)**

Overall order of reaction can be decided by the data given $t_{75\%} = 2t_{50\%}$

∴ It is a first order reaction with respect to P.

From graph [Q] is linearly decreasing with time, i.e. order of reaction with respect to Q is zero and the rate expression is r = k $[P]^1[Q]^0$.

Hence (D) is correct.

22. Consider the following complex ions, P, Q and R

$$P = \left[FeF_6\right]^{3-}, Q = \left[V\left(H_2O\right)_6\right]^{2+} \text{ and } R = \left[Fe\left(H_2O\right)_6\right]^{2+}$$
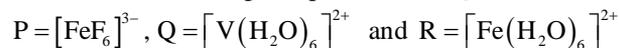
The correct order of the complex ions, according to their spin–only magnetic moment values (in B.M.) is

(A) R < Q < P   (B) Q < R < P
(C) R < P < Q   (D) Q < P < R

Sol. **(B)**

P = Fe^{+3} (no. of unpaired e^- = 5)

Q = V^{+2} (no. of unpaired e^- = 3)

R = Fe^{+2} (no. of unpaired e^- = 4)

As all ligands are weak field, hence the no. of unpaired electrons remains same in the complex ion.

$$\mu = \sqrt{n\left(n+2\right)} \text{ B.M.}$$

Hence (B) is correct.

23. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is
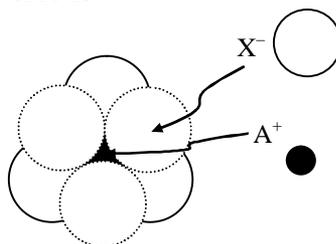
(A) 104 pm   (B) 125 pm
(C) 183 pm   (D) 57 pm

Sol.   **(A)**

According to the given figure, A^+ is present in the octahedral void of X^-. The limiting radius in octahedral void is related to the radius of sphere as

$r_{void} = 0.414\ r_{sphere}$

$r_{A^+} = 0.414 r_{X^-}$

$\quad = 0.414 \times 250$ pm $= 103.5$

$\quad \approx 104$ pm

Hence (A) is correct.

24. Concentrated nitric acid, upon long standing, turns yellow–brown due to the formation of
(A) NO   (B) NO_2
(C) N_2O (D) N_2O_4

Sol.   **(B)**

$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$

NO_2 remains dissolved in nitric acid colouring it yellow or even red at higher temperature.

25. The compound that does NOT liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is
(A) Benzoic acid   (B) Benzenesulphonic acid
(C) Salicylic acid   (D) Carbolic acid (Phenol)

Sol.   **(D)**

pK_a of PhOH (carbolic acid) is 9.98 and that of carbonic acid (H_2CO_3) is 6.63 thus phenol does not give effervescence with HCO_3^- ion.

26. Sulfide ores are common for the metals
(A) Ag, Cu and Pb   (B) Ag, Cu and Sn
(C) Ag, Mg and Pb   (D) Al, Cu and Pb

Sol.   **(A)**

Sulfide ore of Ag → Argentite (Ag_2S), Pb → Galena (PbS), Cu → Copper glance (Cu_2S)
Hence (A) is correct.

27. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25^0C. For this process, the correct statement is
(A) The adsorption requires activation at 25^0C.
(B) The adsorption is accompanied by a decrease in enthalpy.
(C) The adsorption increases with increase of temperature.
(D) The adsorption is irreversible.

Sol.   **(B)**

Adsorption of methylene blue on activated charcoal is physical adsorption hence it is characterised by decrease in enthalpy. Hence (B) is correct.

28. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as

H_3C-Cl <image: isopropyl chloride structure> —Cl   <image: allyl chloride structure> Cl   <image: phenacyl chloride structure> Cl
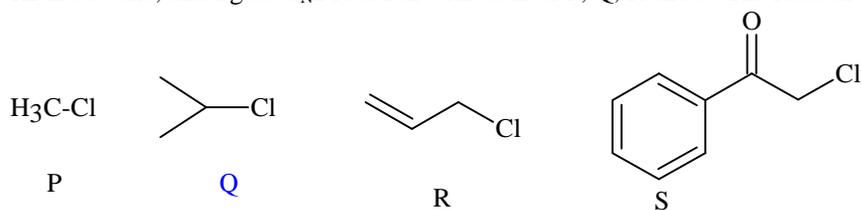
     P   Q   R   S

(A) P > Q > R > S   (B) S > P > R > Q
(C) P > R > Q > S   (D) R > P > S > Q

Sol. **(B)**

Relative reactivity for S_N2 reaction in the given structures is
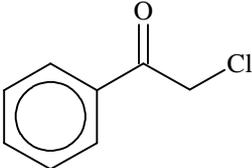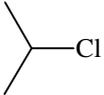
Substrate	<image: phenacyl chloride structure> (S)	CH_3Cl (P)	$H_2C{=}CH{-}CH_2Cl$ (R)	<image: isopropyl chloride structure> —Cl (Q)
Relative Rates Towards S_N2	100000	200	79	0.02

*29. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25^0C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25^0C is

(A) +2900 kJ   (B) – 2900 kJ
(C) –16.11 kJ   (D) +16.11 kJ

Sol. **(C)**

Combustion of glucose

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

$\Delta H_{combustion} = \left(6 \times \Delta H_f CO_2 + 6 \times \Delta H_f H_2O\right) - \Delta H_f C_6H_{12}O_6$

= (6 × - 400 + 6 × - 300) – (- 1300)
= - 2900 kJ/mol
= - 2900/180 kJ/g
= - 16.11 kJ/g

Hence (C) is correct.

30. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulfide is

(A) Fe(III)   (B) Al(III)
(C) Mg(II)   (D) Zn(II)

Sol. **(D)**

Among Fe^{3+}, Al^{3+}, Mg^{2+}, Zn^{2+} only Zn^{2+} is precipitated with ammonical H_2S as ZnS.

SECTION – 2
(One or More Options Correct Type)

This section contains **5 multiple choice questions.** Each question has four choices (A), (B), (C) and (D) out of which **ONE or MORE** are correct.

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*31. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is
(A) 1×10^{-4} (B) 1×10^{-5}
(C) 1×10^{-6} (D) 1×10^{-3}

Sol. **(A)**

Rate in weak acid $= \dfrac{1}{100}\left(\text{rate in strong acid}\right)$

$\therefore$ $\left[H^+\right]_{\text{weak acid}} = \dfrac{1}{100}\left[H^+\right]_{\text{strong acid}}$

$\therefore$ $\left[H^+\right]_{\text{weak acid}} = \dfrac{1}{100}M = 10^{-2}M$

$\therefore$ $C\alpha = 10^{-2}$

$\therefore$ $K_a = 10^{-4}$

Option (A) is correct.

*32. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to
(A) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations. (B) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations.
(C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations. (D) $p(\text{filled}) \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations.

Sol. **(A)**
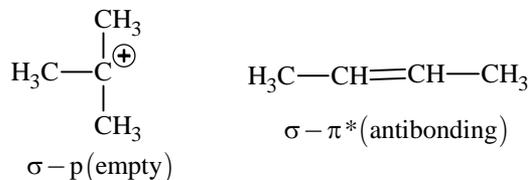
33. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are)
(A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$ (B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$ (D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

Sol. **(B, D)**

$\left[Co\left(NH_3\right)_4 Cl_2\right]^+$ (an octahedral complex) and $\left[Pt\left(NH_3\right)_2\left(H_2O\right)Cl\right]^+$ (a square planar complex) will show geometrical isomerism.

$\left[Pt\left(NH_3\right)_3\left(NO_3\right)\right]Cl$ and $\left[Pt\left(NH_3\right)_3 Cl\right]Br$ will show ionization isomerism.

*34. Among **P, Q, R** and **S,** the aromatic compound(s) is/are
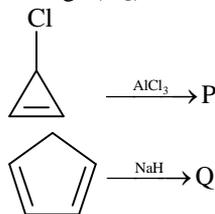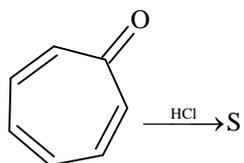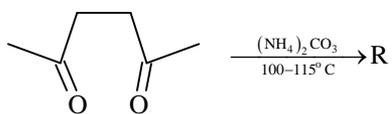
(A) P   (B) Q

(C) R   (D) S

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

Mechanism

$$(NH_4)_2 CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$$

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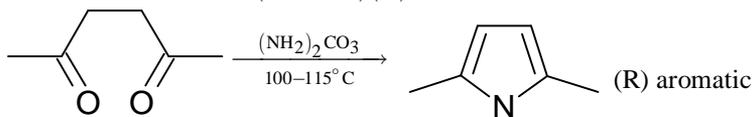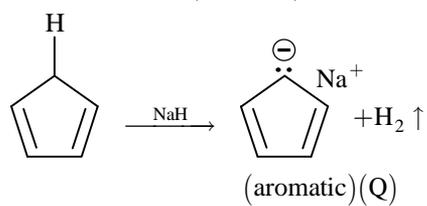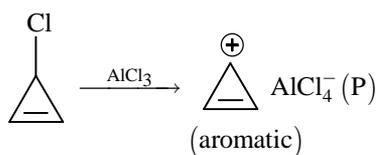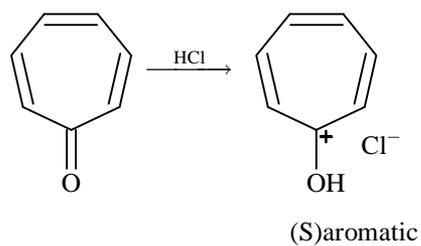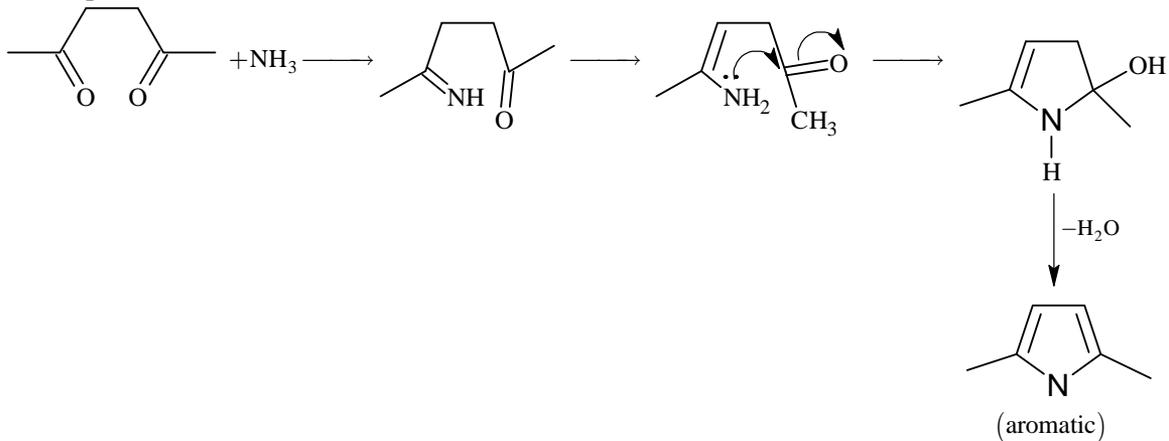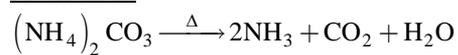
35. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)

(A) ΔG is positive
(B) ΔS_{system} is positive

(C) $\Delta S_{surroundings} = 0$
(D) $\Delta H = 0$

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

For ideal solution, $\Delta S_{system} > 0$

$$\Delta S_{surrounding} = 0$$

$$\Delta H_{mixing} = 0$$

SECTION-3 (Integer value correct Type)

This section contains **5** questions. The answer to each of the questions is a **single digit integer,** ranging from 0 to 9. (both inclusive).

*36. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at -73°C is "M" times that of the de Broglie wavelength of Ne at 727° C. M is

Sol. **(5)**

Since, $\lambda = \dfrac{h}{mV} = \dfrac{h}{\sqrt{2M \ K.E}}$ (since K.E. $\propto$ T)

$\Rightarrow \qquad \lambda \propto \dfrac{1}{\sqrt{MT}}$

For two gases,

$\dfrac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\dfrac{M_{Ne} T_{Ne}}{M_{He} T_{He}}} = \sqrt{\dfrac{20}{4} \times \dfrac{1000}{200}}$

37. EDTA^{4-} is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in $[Co(EDTA)]^{1-}$ complex ion is

Sol. **(8)**
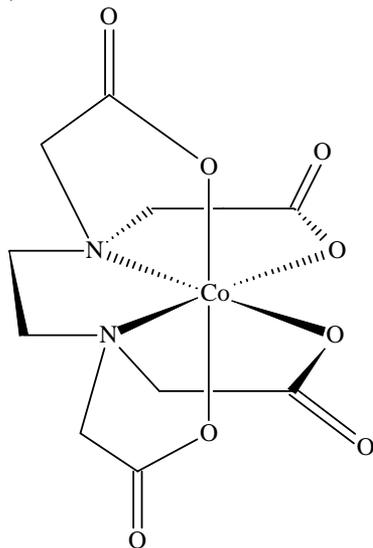
Total no. of N – Co – O bond angles is 8.

38. The total number of carboxylic acid groups in the product **P** is

$$\xrightarrow[\substack{2.\ O_3 \\ 3.\ H_2O_2}]{1.\ H_3O^+,\Delta} P$$
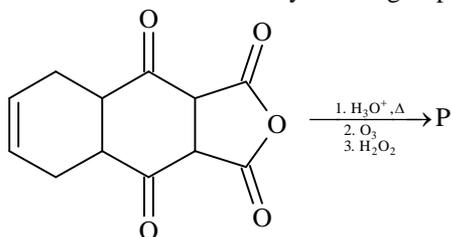
Sol. **(2)**
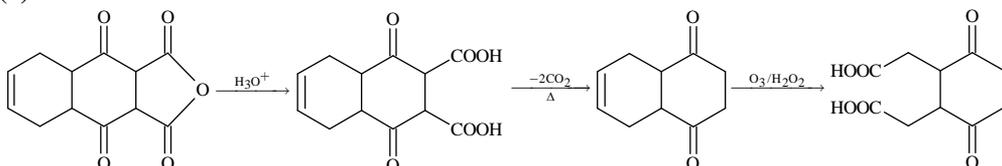
39. A tetrapeptide has – COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with – NH_2 group attached to a chiral center is

Sol. **(4)**

Because –COOH group of tetrapeptide is intact on alanine, its NH_2 must be participating in condensation.

∴ Alanine is at one terminus, − − − A.

To fill the 3 blanks, possible options are:

(i) When NH_2 group attached to non chiral carbon

G	V	P
G	P	V
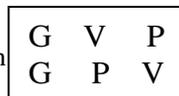
(ii) When NH_2 group attached to chiral carbon

V	G	P		P	V	G
V	P	G		P	G	V
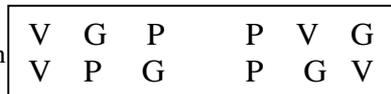
where, Glycine (G)
Valine (V)
Phenyl alanine (P)
Alanine (A)

So the number of possible sequence are 4.

40. The total number of lone-pairs of electrons in melamine is

Sol. **(6)** lone pairs

Melamine