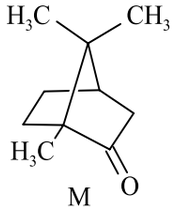
JEE ADVANCED 2015: PAPER–I
(MODEL SOLUTIONS)

SECTION I

(Single Digit Integer Type)

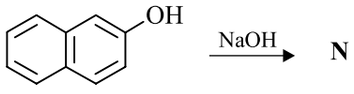
This section contains **EIGHT** questions.
This answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive

1. The total number of stereoisomers that can exist for **M** is _____.



M

2. The number of resonance structures for **N** is



N

3. The total number of lone pairs of electrons in N_2O_3 is _____ .

4. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is _____.

[Atomic number of Fe = 26]

5. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is _____.

[Atomic number: S = 16, Cl = 17, I = 53 and Xe = 54]

6. Not considering the electronic spin, the degeneracy of the second excited state (n = 3) of H atom is 9, while the degeneracy of the second excited state of H^- is _____ .

7. All the energy released from the reaction X $\rightarrow$ Y, ΔG^o = – 193 kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, E^o = – 0.25V.

Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is _____ . [$1F$ = 96500 C mol^{-1}]

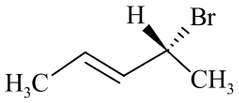
8. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is – 0.0558 ºC, the number of chloride(s) in the coordination sphere of the complex is _____.

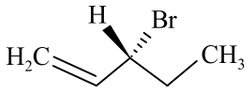
[K_f of water = 1.86 K kg mol^{-1}]

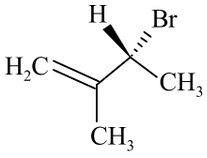
SECTION II
(One or More than One Options Correct Type)

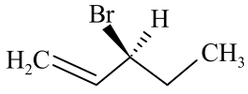
This section contains **TEN** questions
Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options(s) is (are) correct

9. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are)

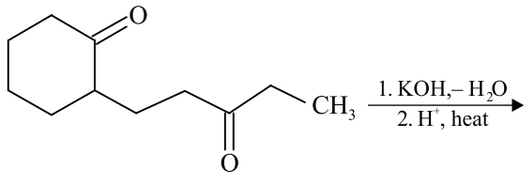
(a) 

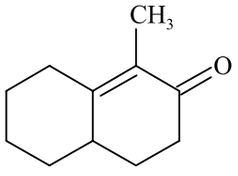
(b) 

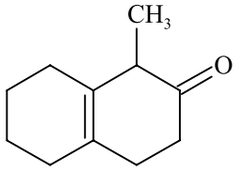
(c) 

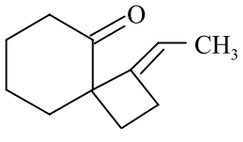
(d) 

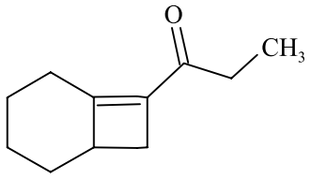
10. The major product of the following reaction is



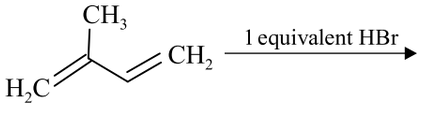
(a) 

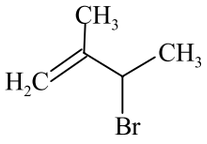
(b) 

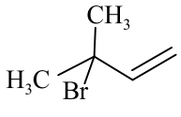
(c) 

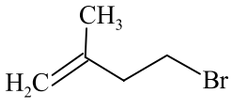
(d) 

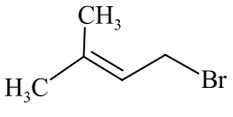
11. In the following reaction, the major product is

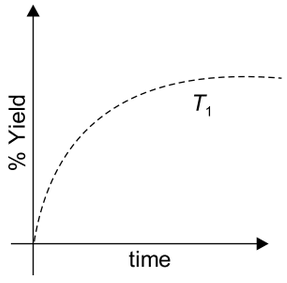


(a) 

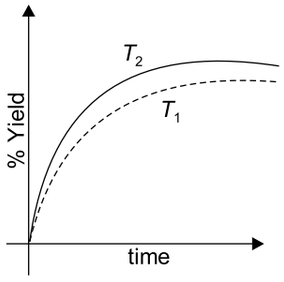
(b) 

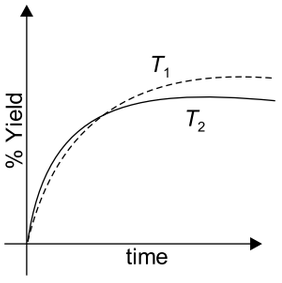
(c) 

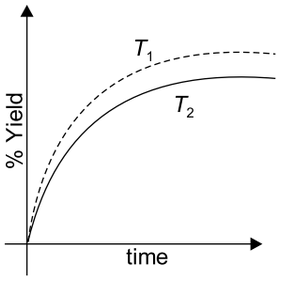
(d) 

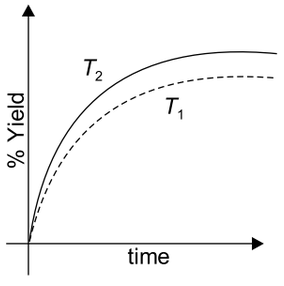


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by

(a)


(b)


(c)


(d)


18. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n, respectively, are

(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

SECTION III

This section contains **TWO** questions

19. Match the anionic species given in Column I with that are present in the ore(s) given in Column II

Column I	**Column II**
(a) Carbonate	(p) Siderite
(b) Sulphide	(q) Malachite
(c) Hydroxide	(r) Bauxite
(d) Oxide	(s) Calamine
	(t) Argentite

20. Match the thermodynamic processes given under Column I with the expressions given under Column II:

Column I	**Column II**
(a) Freezing of water at 273 K and 1 atm	(p) $q = 0$
(b) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(q) $w = 0$
(c) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(r) $\Delta S_{sys} < 0$
(d) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$
	(t) $\Delta G = 0$

ANSWERS

1. (2) **2.** (9) **3.** (8) **4.** (4) **5.** (4)
6. (3) **7.** (4) **8.** (1) **9.** (b), (d) **10.** (a)
11. (d) **12.** (a) **13.** (c) **14.** (a), (b), (c) **15.** (b), (c), (d)
16. (a), (b) **17.** (c) **18.** (a)

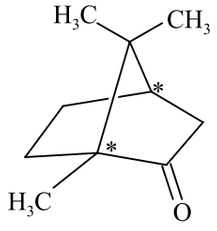
19. The correct-bubbled diagram is as follows.

A	**p**	**q**	r	**s**	t
B	p	q	r	s	**t**
C	p	**q**	**r**	s	t
D	p	q	**r**	s	t

20. (a) ↔ (r), (t); (b) ↔ (p), (q), (s);(c) ↔ (p), (q), (s);(d) ↔ (p), (q), (s), (t)

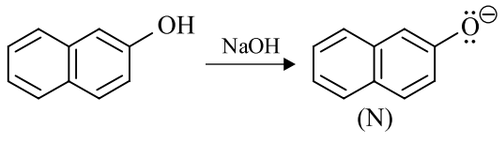
Solutions

1. There are two asymmetric carbon atoms in the molecule.

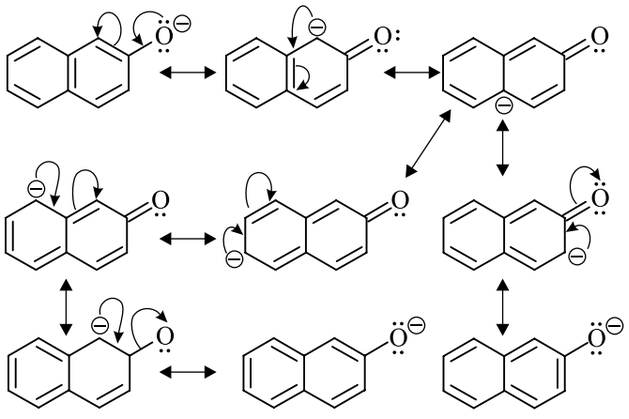


Due to rigid bridged-bicyclic compound, the number of isomers observed is 2 instead of four.

2. The reaction is

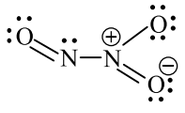


The resonating structures of N are as follows:



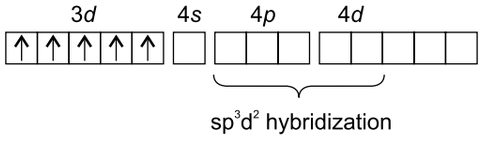
There are 9 resonating structures.

3. The structure of N_2O_3 is



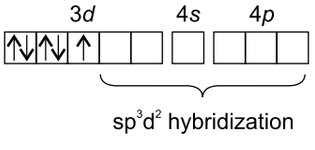
There are 8 pairs of lone electrons in N_2O_3.

4. SCN^- being a weak ligand, it will form high-spin complex with Fe^{3+} ($3d^5$) ion.
Fe^{3+} *in* $[Fe(SCN)_6]^{3-}$



Its spin only magnetic moment will be $\mu = \sqrt{n(n+2)}\,\mu_B = \sqrt{5(7)}\,\mu_B = 5.92\,\mu_B$

CN^- being a strong ligand, it will form low-spin complex with Fe^{3+} ion.
Fe^{3+} in $[Fe(CN)_6]^{3-}$

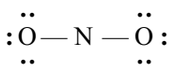
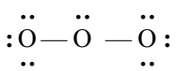
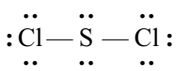
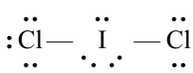
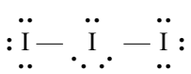
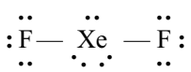


Its spin-only magnetic moment will be $\mu = \sqrt{n(n+2)}\,\mu_B = \sqrt{1(3)}\,\mu_B = 1.73\,\mu_B$

The difference between the two magnetic moment is $\Delta\mu = (5.92 - 1.73)\ \mu_B = 4.19\ \mu_B \simeq 4\ \mu_B$ (nearest integer)

5. The valence electrons, their distributions, involved hybridization of the central atom in the given molecules/ ions are as follows.

$BeCl_2$	2+2×7=16	:Cl—Be—Cl:	sp linear
N_3^-	3×5+1=16	:N—N—N:	sp linear
NO_2	2×5+6=16	:N—N—O:	sp linear

NO_2^+	5+2×6–1=16		sp linear
O_3	3×6=18		sp^2 Nonlinear
SCl_2	6+2×7=20		sp^3 Nonlinear
ICl_2^-	7+2×7+1=22		dsp^3 Nonlinear
I_3^-	3×7+1=22		dsp^3 Nonlinear
XeF_2	8+2×7=22		dsp^3 Nonlinear

There are **four** molecules/ion(s) which are linear without involving d orbitals in hybridization.

6. For one-electron species, the energy of electron is governed by the principal quantum number n while for the multi-electron species, the energy is governed by the sum of principal and azimuthal quantum numbers (i.e. $n + l$)

In H atom, for $n = 3$, the degeneracy is 9 involving 3s, three 3p orbitals and five 3d orbitals.

In H^- ion, the second excited state is 2p orbitals and their degeneracy is **three**.

7. The free energy change involved in the reaction $M^{3+} \rightarrow M^{3+} + 2e^-$ is

$$\Delta G^\circ = -nFE^\circ = -(2)\ (96500\ \text{C mol}^{-1})\ (-0.25\ \text{V})$$
$$= 48250\ \text{J mol}^{-1}$$

The number of moles of M^+ oxidized is

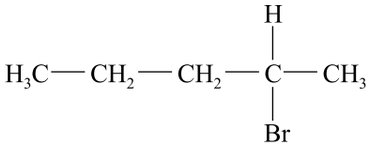
$$n = \frac{-\Delta G^o(\text{X} \rightarrow \text{Y})}{\Delta G^o(\text{M}^+ \rightarrow \text{M}^{3+})} = \frac{193 \times 10^3\ \text{J mol}^{-1}}{48250\ \text{J mol}^{-1}} = 4$$

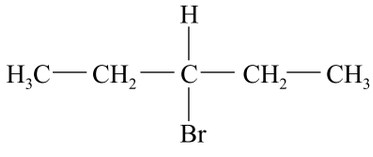
8. For an electrolyte, the van't Hoff factor is defined as

$$i = i - \frac{\Delta T_f}{K_f m} = \frac{0.0558\,\text{K}}{(1.86\,\text{K kg mol}^{-1})\ (0.01\ \text{mol kg}^{-1})} = 3$$

From this, it follows that the complex is $[Co(NH_3)_5Cl]Cl_2$ as it gives three species in the solution. Hence, the number of chloride within the coordination sphere is 1.

9. The hydrogenated products are:

(a)  Optically active

(b)  Optically inactive