JEE (ADVANCED) 2018 PAPER-1

[PAPER WITH SOLUTION]

HELD ON SUNDAY 20TH MAY, 2018

CHEMISTRY

SECTION 1 (Maximum Marks : 24)

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	: **+4**	If only (all) the correct option(s) is (are) chosen.
Partial Marks	: **+3**	If all the four options are correct but ONLY three options are chosen.
Partial Marks	: **+2**	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	: **+1**	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	: **0**	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	: **–2**	In all other cases.

- **For example :** If If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in -2 marks.

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1. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)

(A) NH_4NO_3

(B) $(NH_4)_2Cr_2O_7$

(C) $Ba(N_3)_2$

(D) Mg_3N_2

1. (B,C)

Below 300ºC ;

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 2H_2O + Cr_2O_3$

$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$Mg_3N_2 \xrightarrow{\Delta 300°C} \text{Do not decompose}$

2. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)

(Atomic numbers: Fe = 26, Ni = 28)

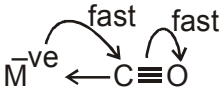
(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16

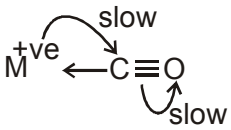
(B) These are predominantly low spin in nature

(C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered

(D) The carbonyl C−O bond weakens when the oxidation state of the metal is increased

2. (B,C)

- Both $[Fe(CO)_5]$ and $[Ni(CO)_4]$ has 18 valence electron
- Ligand field strength α pairing of unpaired electron.
- 

- 

3. Based on the compounds of group 15 elements, the correct statement(s) is (are)

(A) Bi_2O_5 is more basic than N_2O_5

(B) NF_3 is more covalent than BiF_3

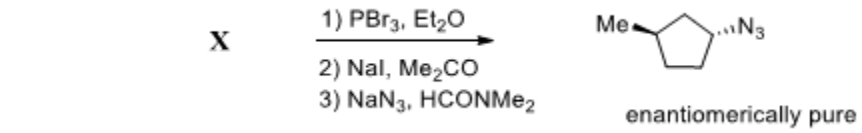
(C) PH_3 boils at lower temperature than NH_3

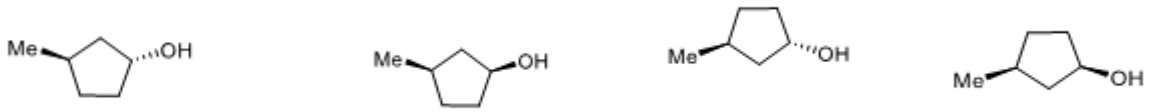
(D) The N−N single bond is stronger than the P-P single bond

3. (A,B,C)

- $N_2O_5 > P_4O_{10} > As_4O_{10} > Sb_4O_{10} > Bi_2O_5$ (Acidic nature)
- NF_3 is more covalent than BiF_3 because both N and F are non-metal
- $NH_3 > PH_3$ (due to H-bond)

4. In the following reaction sequence, the correct structure(s) of **X** is (are)

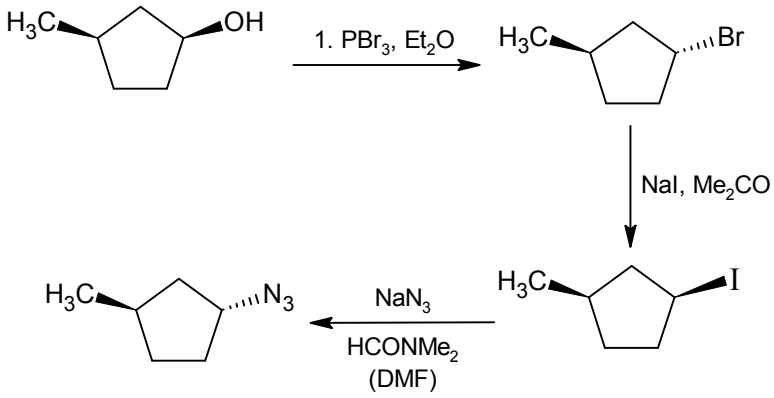




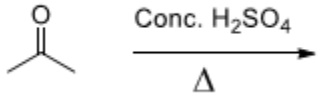
(A) (B) (C) (D)

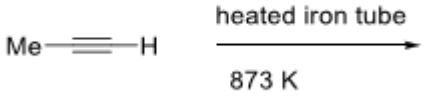
Ans. (B)

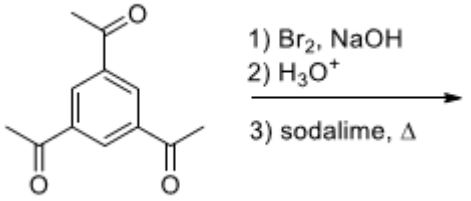
Sol.

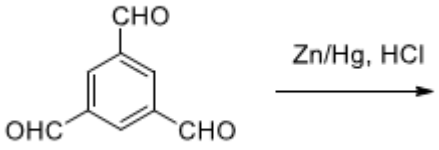


5. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

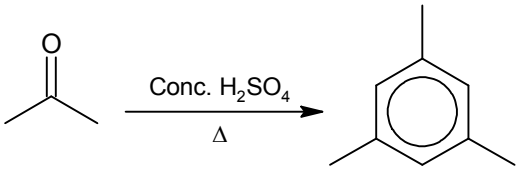
(A) 

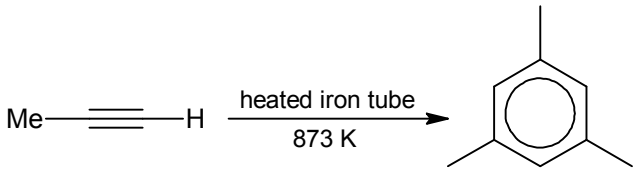
(B) 

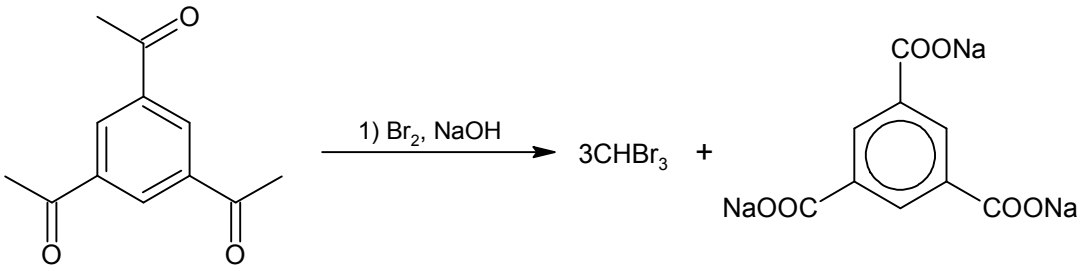
(C) 

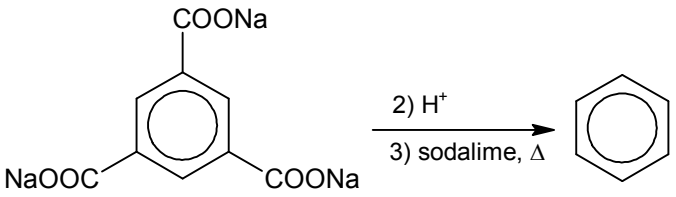
(D) 

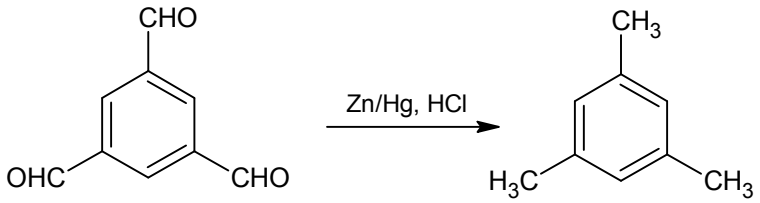
Ans. (A, B, D)

Sol. (A) 

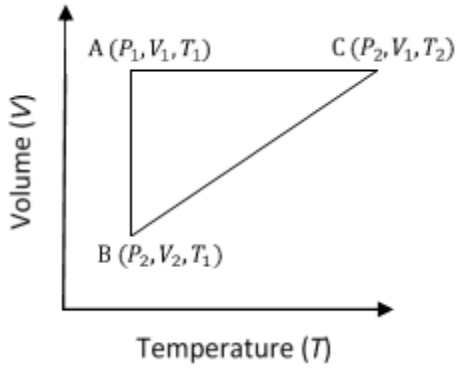
(B) 

(C) 



(D) 

6. A reversible cyclic process for an ideal gas is shown below. Here, *P*, *V*, and *T* are pressure,volume and temperature, respectively. The thermodynamic parameters *q*, *w*, *H* and *U* are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are)

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(B) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Ans. (B, C)

Sol.

AB	AC	BC
$W_{AB} = -n\,RT_1\,\ln\frac{V_2}{V_1}$	$W_{AC} = 0$	$W_{BC} = -P_2(V_1 - V_2)$
$q_{AB} = +nRT_1\,\ln\frac{V_2}{V_1}$	$q_{AC} = nC_{V,m}(T_2 - T_1)$	$= P_2(V_2 - V_1)$
$\Delta H_{AB} = 0$	$\Delta U_{AC} = nC_{V,m}(T_2 - T_1)$	$q_{BC} = nC_{p,m}(T_2 - T_1)$
$\Delta U_{AB} = 0$	$\Delta H_{AC} = nC_{P,m}(T_2 - T_1)$	$\Delta H_{BC} = nC_{p,m} = (T_2 - T_1)$
		$\Delta U_{BC} = nC_{V,m}(T_2 - T_1)$

(A) $q_{AC} = \Delta U_{BC}$: $W_{AB} \neq P_2(V_2 - V_1)$ Incorrect.

(B) $W_{BC} = P_2(V_2 - V_1)$, $q_{BC} = \Delta H_{AC}$ correct

(C) $C_{pm} > C_{v,m}$; $\Delta H_{CA} = nC_{p,m}(T_1 - T_2) < 0$

$\Delta U_{CA} = nC_{v,m}(T_1 - T_2) < 0$

$\Delta H_{CA} < \Delta U_{CA}$, $q_{AC} = \Delta U_{BC}$; correct

(D) $q_{BC} = \Delta H_{AC}$; $\Delta H_{CA} < \Delta U_{CA}$; incorrect

SECTION 2 (Maximum Marks : 24)

- This section contains **EIGHT (08)** 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, 30.27, -127.30) using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : **+3** If ONLY the correct numerical value is entered as answer.

  Zero Marks **: 0** In all other cases.

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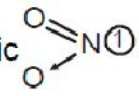
7. Among the species given below, the total number of diamagnetic species is ___.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase,

Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

Ans. (1.00)

Sol.

- $Mn_3O_4 \Rightarrow 2\overset{+2}{Mn}O.\overset{+4}{Mn}O_2 \Rightarrow$ Paramagnetic
- H-atom $\rightarrow$ Paramagnetic
- NO_2 Paramagnetic  $\Rightarrow$ Paramagnetic

- $O_2^- \rightarrow$ unpaired electron = 1 $\Rightarrow$ Paramagnetic
- $S_2(g) \rightarrow$ unpaired electrons = 2 $\Rightarrow$ Paramagnetic like O_2
- $(NH_4)_2[\overset{+2}{F}eCl_4] \Rightarrow$ configuration is $3d^6$

  $\therefore$ unpaired electron = 4 $\Rightarrow$ Paramagnetic
- $(NH_4)_2[NiCl_4) \Rightarrow$ configuration $\Rightarrow 3d^8$

  $\Rightarrow$ Unpaired electrons = 2 $\Rightarrow$ Paramagnetic
- $K_2\overset{+6}{M}nO_4 \Rightarrow$ configuration = $3d^1 \Rightarrow$ Paramagnetic

  $K_2\overset{+6}{C}rO_4 \Rightarrow$ configuration = $3d^0 \Rightarrow$ Diamagnetic

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2.6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $NiCl_2.6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickelammonia coordination compound thus produced is ____.

(Atomic weights in g mol-1: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

Ans. (2992.00)

Sol. $(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2NH_3 + CaSO_4 \cdot 2H_2O$

$$\text{mole of } (NH_4)_2SO_4 = \frac{1584}{132} = 12$$

$$\text{mole of } (NH_3) \text{ formed} = 24$$

Mole of gypsum = 12 mole = 12×172 = 2064 g

$$\underset{4 \text{ mole}}{NiCl_2 6H_2O} + \underset{24 \text{ mole}}{6NH_3} \rightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

$$\text{moles of } NiCl_2 6H_2O = \frac{952}{238} = 4 \text{ mole}$$

$$\text{moles of } [Ni(NH_3)_6Cl_2 = \frac{24}{6} = 4 \text{ mole} = 4 \times 232\,g = 928\,g$$

Total required mass = 2064 + 928 = 2992 g.

9. Consider an ionic solid **MX** with NaCl structure. Construct a new structure **(Z)** whose unit cell is constructed from the unit cell of **MX** following the sequential instructions given below. Neglect the charge balance.

(i) Remove all the anions **(X)** except the central one

(ii) Replace all the face centered cations **(M)** by anions **(X)**

(iii) Remove all the corner cations **(M)**

(iv) Replace the central anion **(X)** with cation **(M)**

$$\text{The value of } \left(\frac{\text{number of anions}}{\text{number of cations}}\right) \text{ in } \mathbf{Z} \text{ is } \_\_\_\_ .$$

Ans. (3.00)

Sol. $X^- \Rightarrow O.V$

$M^+ \Rightarrow fcc$

	M^+	X^-
(i)	4	1
(ii)	$4-3$	$3+1$
(iii)	$4-3-1$	$3+1$
(iv)	1	3

$$Z = \frac{3}{1} = 3$$

10. For the electrochemical cell,

$$Mg(s) \mid Mg^{2+}(aq, 1\ M) \parallel Cu^{2+}(aq, 1\ M) \mid Cu(s)$$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to **x** M, the cell potential changes to 2.67 V at 300 K. The value of **x** is ____.

(Given, $\frac{F}{R} = 11500\ K\ V^{-1}$, where F is the Faraday constant and R is the gas constant, ln(10) = 2.30)

Ans. (10.00)

Sol. $E_{cell} = E^{o}_{cell} - \frac{RT}{2F} \ln \frac{Mg^{++}}{Cu^{++}}$

$$2.67 = 2.70 - \frac{300}{2 \times 11500} \ln x$$

$$\ln x = \frac{0.03 \times 2 \times 11500}{300}$$

$$\ln x = 2.30$$

$$X = 10$$

11. A closed tank has two compartments **A** and **B**, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator **(Figure 1)**. If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across **(Figure 2)**, the volume (in m^3) of the compartment

A after the system attains equilibrium is ____.

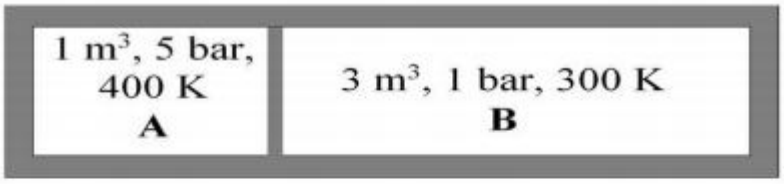


Figure 1

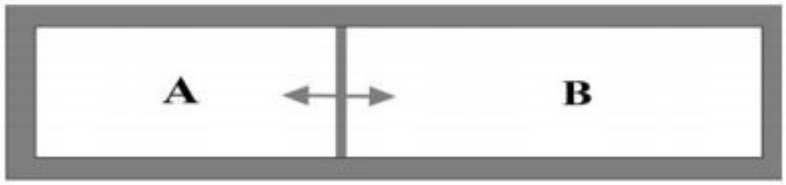


Figure 2

Ans. (2.22)

Sol. Initially; no of moles of O_2 in compartment

$$A;\ n_A = \frac{P_1V_1}{RT_1}$$

And no. of moles of O_2 in

$$\text{compartment B, } n_B = \frac{P_2V_2}{RT_2}$$

$$\text{i.e., } \frac{n_A}{n_B} = \frac{P_1V_1}{T_1} / \frac{P_2V_2}{T_2} = \frac{5\times1}{400} / \frac{1\times3}{300} = \frac{5}{4}$$

In final condition when the system attains equilibrium, both pressure and T will be same in the two compartment A and B

$$\text{so, } V \propto n$$

$$\text{i.e., } \frac{V_A}{V_B} = \frac{n_A}{n_B} = \frac{5}{4}$$

Now, as total volume of system

= 1+3=4 m^3

$$V_A = \frac{5}{9}\times 4m^3 = \frac{20}{9}m^3 = 2.22\ m^3$$

12. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids **A** and **B** has vapour pressure 45 Torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is ____.

(given that the vapour pressure of pure liquid **A** is 20 Torr at temperature T)

Ans. (19.00)

Sol. $p_A^o = 20 \text{ mm}$

$$p_T = p_A^o \, x_A + p_B^o \cdot x_B$$

$$45 = 20 \times \frac{1}{2} + p^oB \times \frac{1}{2}$$

$$p_B^o = 70$$

$$22.5 = 20 \cdot x_A + 70(1 - x_A)$$

$$x_A = \frac{47.5}{50}$$

$$1 - x_A = x_B = \frac{2.5}{50}$$

$$\text{Ratio } \frac{x_A}{x_B} = \frac{47.5}{2.5} = 19$$

13. The solubility of a salt of weak acid (**AB**) at pH 3 is **Y**×10^{-3} mol L^{-1}. The value of **Y** is ____.

(Given that the value of solubility product of **AB** (K_{sp})=2×10^{-10} and the value of ionization constant of **HB** (K_a)=1×10^{-8}

Ans. (4.47)

Sol. Let solubility of AB is S

$$AB \rightleftharpoons A^+ + B^-, \quad B^- + H^+ \rightleftharpoons HB$$

$$Ksp = [A^+][B^-] \qquad \ldots(i)$$

$$S = [B^-] + HB \text{ (mass balance)}$$

$$S = B^- + \frac{[H^+][B^-]}{K_a}$$

$$S = B^- \times \left[1 + \frac{H^+}{Ka}\right]$$

$$S = \frac{Ksp}{[A^+]}\left[1+\frac{H^+}{Ka}\right]$$

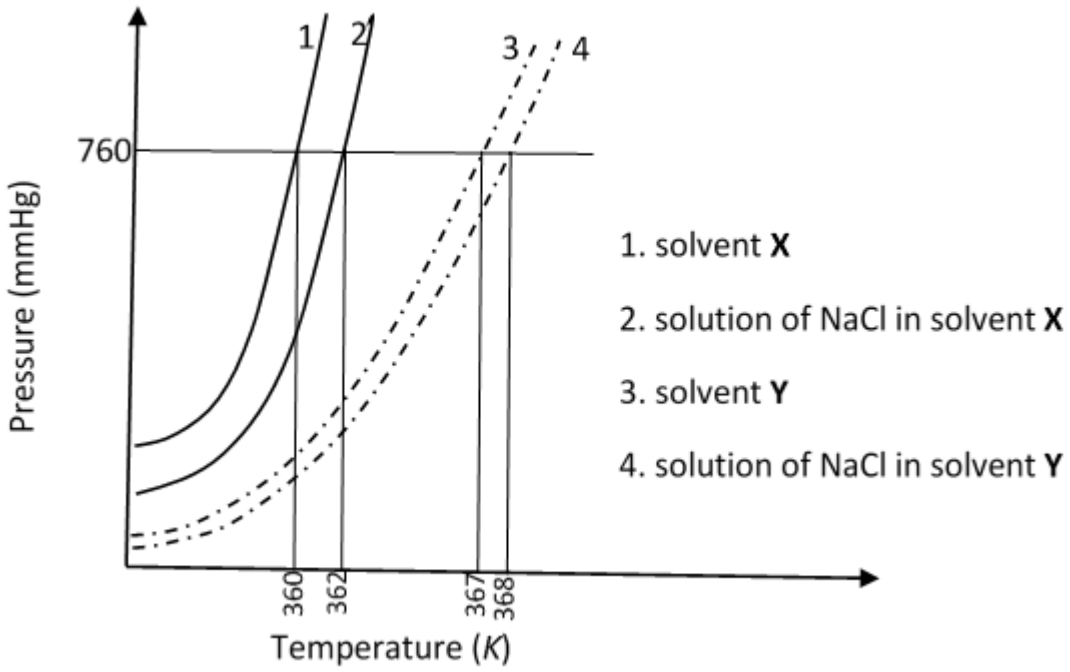
$$S = \frac{Ksp}{S}\left[1+\frac{H^+}{Ka}\right]$$

$$S = \sqrt{Ksp\left[1+\frac{H^+}{Ka}\right]}$$

$$S = \sqrt{2\times10^{-10}\left(1+\frac{10^{-3}}{10^{-8}}\right)} = 4.47\times10^{-3}$$

Y = 4.47

14. The plot given below shows P – T curves (where *P* is the pressure and *T* is the temperature) for two solvents **X** and **Y** and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**.Solute **S** is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is ____.

Ans. **(0.05)**

Sol. $(\Delta T_b)_x = (K_b)_x \cdot m \times 2$ [i = 2 for NaCl]

$$(K_b)_x^m = \frac{2}{2} = 1$$

$$(\Delta T_b)_y = (K_b)_y \; m \times 2$$

$$(K_b)_y^{\;m} = \frac{1}{2} = 0.5$$

$$\frac{(K_b)_x}{(K_b)_y} = \frac{1}{.5} = 2$$

For S

$$(\Delta T_b)_x = 3\,(\Delta T_b)_y$$

$$\text{For dimerzation } i = 1 + \alpha\left(\frac{1}{2} - 1\right)$$

$$\left(1 + \frac{\alpha}{2} - \alpha\right)(K_b)_x^m = 3 \times \left(1 + \frac{0.7}{2} - 0.7\right)(K_b)_y^m$$

$$\left(1 - \frac{\alpha}{2}\right)(K_b)_x = 3x\left(1 - \frac{0.7}{2}\right)(K_b)_y$$

$$1 - \frac{\alpha}{2} = \frac{3 \times 1.3}{2} \times \frac{(K_b)_y}{(K_b)_x}$$

$$1 - \frac{\alpha}{2} = \frac{3.9}{2} \times \frac{1}{2} = 0.975 \Rightarrow \alpha = 0.05$$

SECTION 3 (Maximum Marks : 12)

- This section contains **TWO (02)** paragraphs. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options corresponds to the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : **+3** If ONLY the correct option is chosen.

  Zero Marks **: 0** If none of the options is chosen (i.e. the question is unanswered).

  Negative Marks : **–1** In all other cases.

PARAGRAPH "X"

Treatment of benzene with CO / HCl in the presence of anhydrous $AlCl_3$ / CuCl followed by reaction with Ac_2O/ NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes **Y** as the major product. Reaction of **X** with H_2/Pd-C, followed by H_3PO_4 treatment gives **Z** as the major product.

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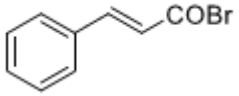
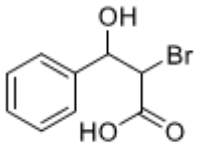
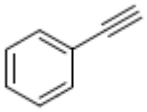
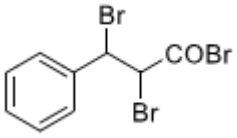
15. The compound **Y** is

(A) 

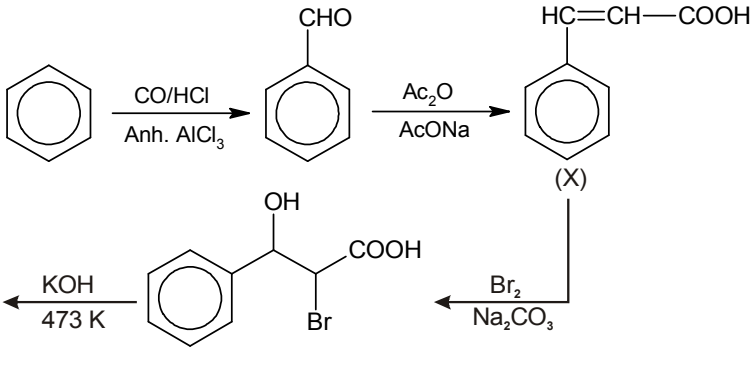
(B) 

(C) 

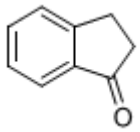
(D) 

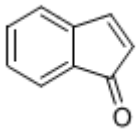
Ans. (C)

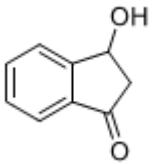
Sol.

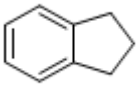


16. The compound **Z** is

(A) 

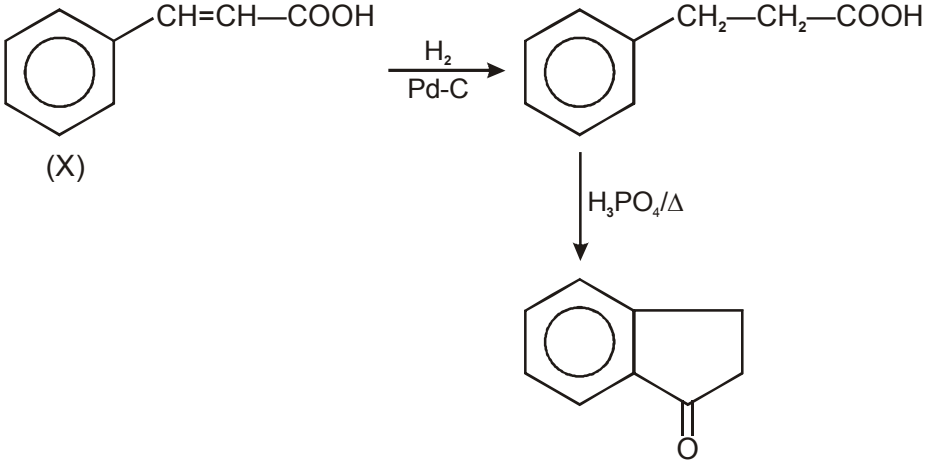
(B) 

(C) 

(D) 

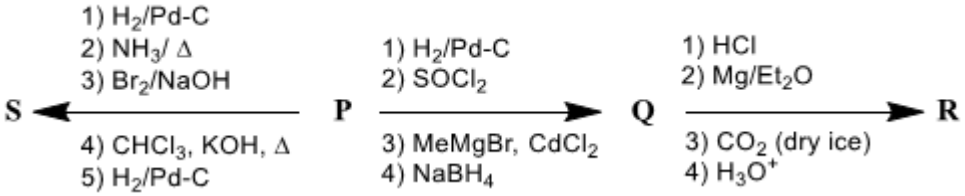
Ans. (A)

Sol.

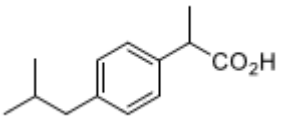


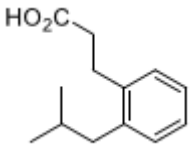
PARAGRAPH "A"

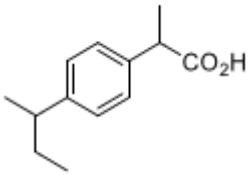
An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q**. The compound P also undergoes another set of reactions to produce **S.**

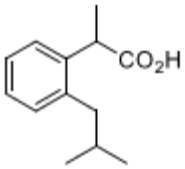


17. The compound **R** is

(A) 

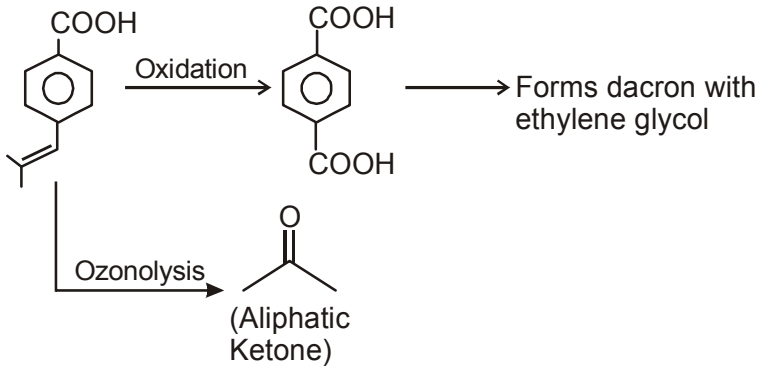
(B) 

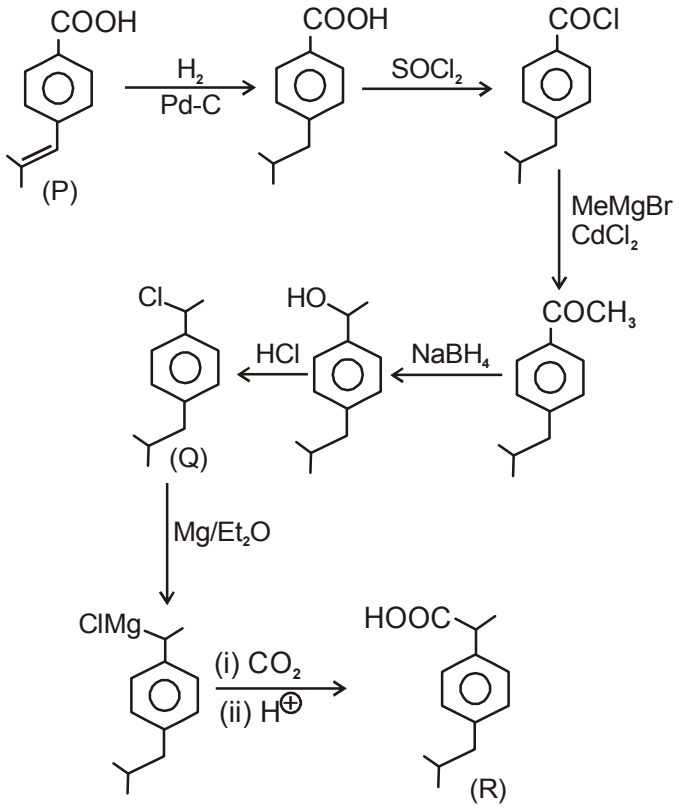
(C) 

(D) 

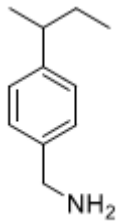
Ans. (A)

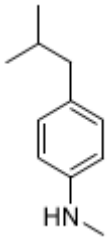
Sol.

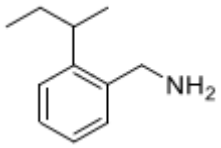


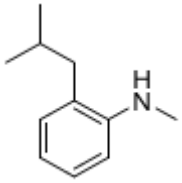


18. The compound **S** is

(A) 

(B) 

(C) 

(D) 

Ans. (B)

Sol.