

SECTION 1 (Maximum Marks: 18)

- This section contains **SIX (06)** questions.
- The answer to each question is a **SINGLE DIGIT INTEGER** ranging from **0 TO 9, BOTH INCLUSIVE**.
- For Each question, enter the correct integer corresponding to the answer 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;
Zero Marks : 0 If the question is unanswered;
Negative Marks : -1 In all other cases.

1. The 1st, 2nd, and the 3rd ionization enthalpies, I_1 , I_2 , and I_3 , of four atoms with atomic numbers n , $n + 1$, $n + 2$, and $n + 3$, where $n < 10$, are tabulated below. What is the value of n ?

Atomic number	Ionization Enthalpy (kJ/mol)		
	I_1	I_2	I_3
n	1681	3374	6050
$n + 1$	2081	3952	6122
$n + 2$	496	4562	6910
$n + 3$	738	1451	7733

Answer: 9

Solution:

According to the tabulated data,

Element with Atomic number ($n + 2$), should be an alkali metal

As we see, first ionization enthalpy (I_1) is very less but second ionization enthalpy (I_2) is very large.

Hence, atomic number can be = 11

That is $n + 2 = 11$

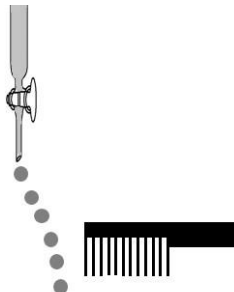
$$n = 9$$

Note: 'n' can't be '1'.

2. Consider the following compounds in the liquid form:

O₂, HF, H₂O, NH₃, H₂O₂, CCl₄, CHCl₃, C₆H₆, C₆H₅Cl.

When a charged comb is brought near their flowing stream, how many of them show deflection as per the following figure?



Answer: 6

Solution:

Only polar molecules are deflected by charged comb.

Polar molecules: HF, H₂O, NH₃, H₂O₂, CHCl₃, C₆H₅Cl

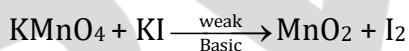
Non-polar molecules: O₂, CCl₄, Benzene

3. In the chemical reaction between stoichiometric quantities of KMnO₄ and KI in weakly basic solution, what is the number of moles of I₂ released for 4 moles of KMnO₄ consumed?

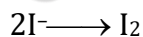
Answer: 6

Solution:

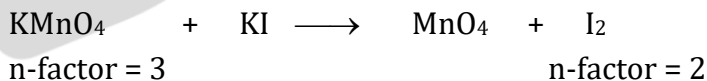
Chemical reaction of KMnO₄ and KI in weakly basic solution is given as



So n-factor of KMnO₄ = 3



n-factor of I₂ is = 2



Equivalents of KMnO₄ = Equivalents of I₂

n-factor × Number of moles (n) = n-factor × Number of moles (n)

3 × moles of KMnO₄ = 2 × moles of I₂

3 × 4 = 2 × moles of I₂

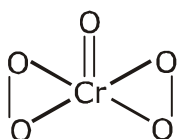
Moles of I₂ = 6 moles

4. An acidified solution of potassium chromate was layered with an equal volume of amyl alcohol. When it was shaken after the addition of 1 mL of 3% H_2O_2 , a blue alcohol layer was obtained. The blue color is due to the formation of a chromium (VI) compound 'X'. What is the number of oxygen atoms bonded to chromium through only single bonds in a molecule of X?

Answer: 4

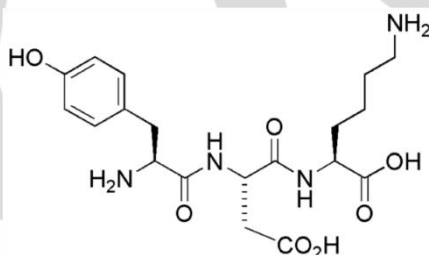
Solution:

Blue colour compound of 'Cr' is CrO_5 .



Oxygen atoms bonded to chromium through only single bonds = 4

5. The structure of a peptide is given below.



If the absolute values of the net charge of the peptide at $\text{pH} = 2$, $\text{pH} = 6$, and $\text{pH} = 11$ are $|z_1|$, $|z_2|$, and $|z_3|$, respectively, then what is $|z_1| + |z_2| + |z_3|$?

Answer: 5

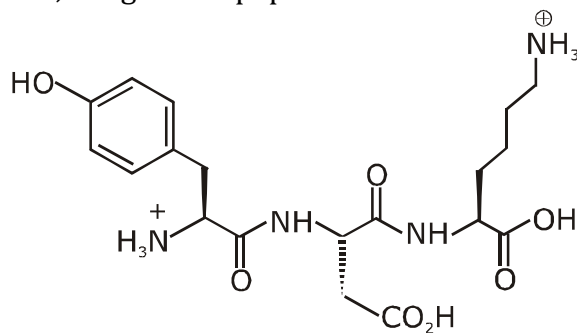
Solution:

(i) At $\text{pH} = 2$ (Highly acidic)

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In highly acidic medium, the given tripeptide exist as cationic form.

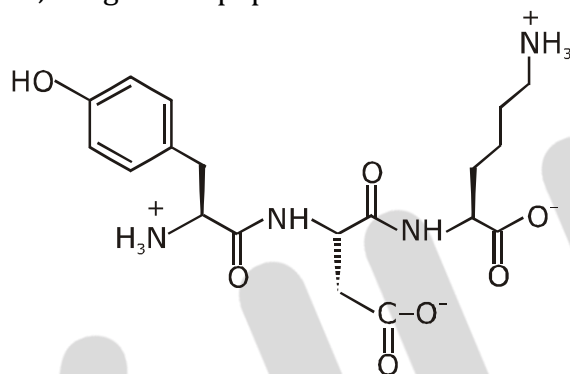


Net charge +2

$|Z_1| = 2$ at pH = 2

(ii) At pH = 6 (neutral solution)

In neutral medium, the given tripeptide exist as Zwitter ion.

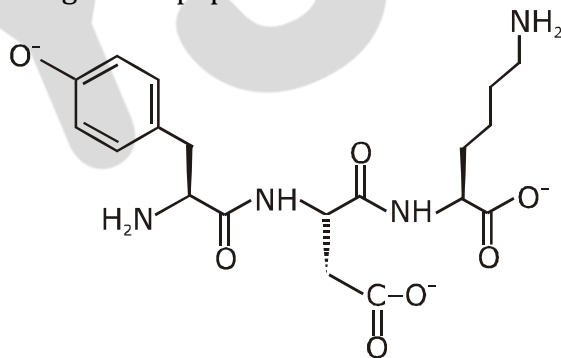


net charge = 0

$|Z_2| = 0$ at pH = 6

(iii) At pH = 11 (basic medium)

In basic medium the given tripeptide exist in anionic form.



Net charge = -3

$|Z_3| = 3$

Therefore $|Z_1| + |Z_2| + |Z_3| = 2 + 0 + 3 = 5$

6. An organic compound ($C_8H_{10}O_2$) rotates plane-polarized light. It produces pink color with neutral $FeCl_3$ solution. What is the total number of all the possible isomers for this compound?

Answer: 6

Solution:

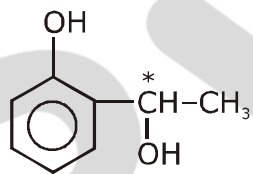
DBE (Double bond equivalent) of $C_8H_{10}O_2$ is

$$= \text{Number of carbon atoms} - (\text{Number of monovalent atoms})/2 + 1$$

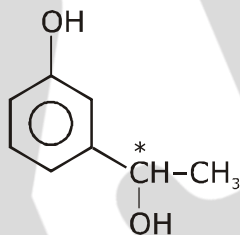
$$= 8 - 10/2 + 1 = 4$$

It gives pink colour with neutral $FeCl_3$ solution. It means phenolic group should be present in the compound.

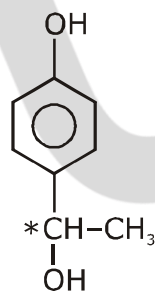
Note: C^* represent chiral carbon. So it will have (d and l) optically active isomers.



(d + l)



(d + l)



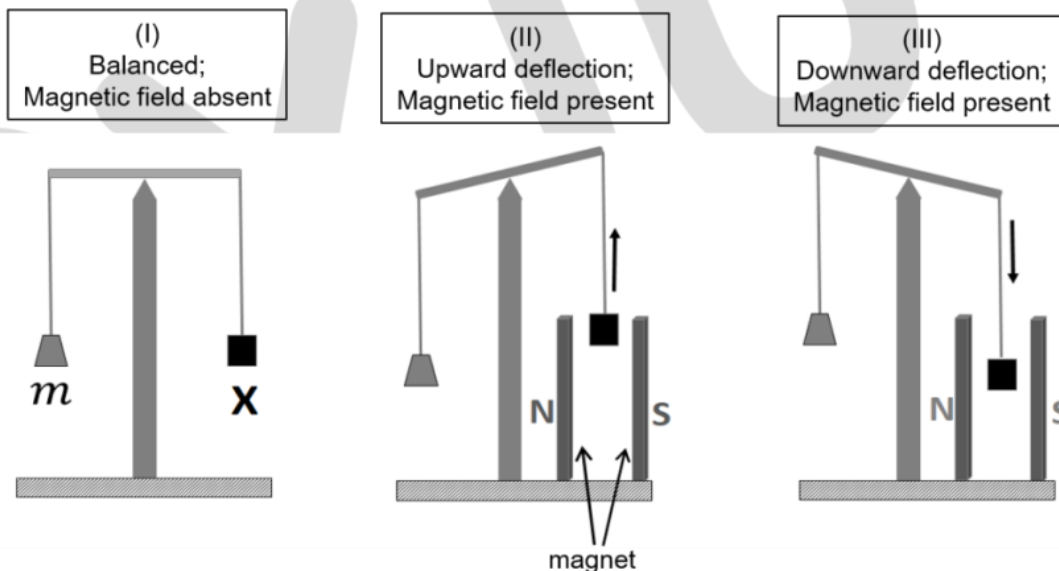
(d + l)

Total optically active isomer = 6

SECTION 2 (Maximum Marks: 24)

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options. **ONE OR MORE THAN ONE** of these four option(s) is(are) the correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- 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 four options is correct but **ONLY** three options are chosen; chosen; both of which are correct;
 - 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 questions is unanswered);
 - Negative Marks* : -2 In all other cases.

7. In an experiment, m grams of a compound **X** (gas/liquid/solid) taken in a container is loaded in a balance as shown in figure I below. In the presence of a magnetic field, the pan with **X** is either deflected upwards (figure II), or deflected downwards (figure III), depending on the compound **X**. Identify the correct statement(s).



- (A) If **X** is $\text{H}_2\text{O}(l)$, deflection of the pan is upwards.
 (B) If **X** is $\text{K}_4[\text{Fe}(\text{CN})_6](s)$, deflection of the pan is upwards.
 (C) If **X** is $\text{O}_2(g)$, deflection of the pan is downwards.
 (D) If **X** is $\text{C}_6\text{H}_6(l)$, deflection of the pan is downwards.

Answer: A, B, C

Solution:

Paramagnetic substances are attracted by magnetic fields & diamagnetic substances are repelled by magnetic field.

O_2 - is paramagnetic

H_2O & $C_6H_6(l)$ - are Diamagnetic

& $K_4[Fe(CN)_6]$ is also Diamagnetic

(A) $x = H_2O \rightarrow$ Diamagnetic

(B) $x = K_4[Fe(CN)_6] \rightarrow$ Diamagnetic

Here, Fe^{+2} strong field ligand.

$\rightarrow 3d^6 \Rightarrow [t_{2g}^6, e_g^0]$

(C) $x = O_2 \rightarrow$ Paramagnetic

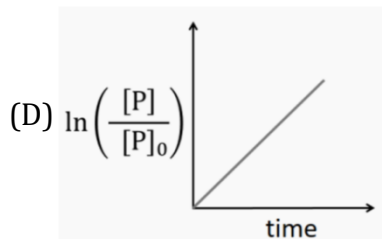
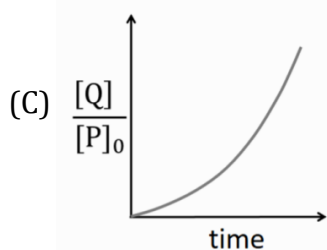
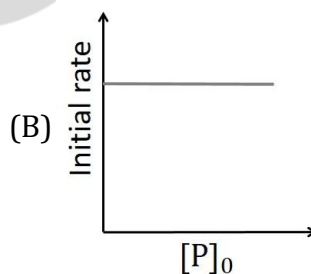
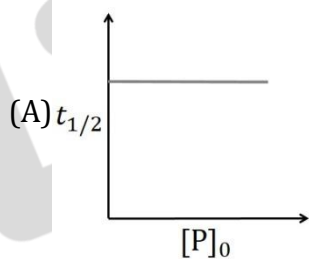
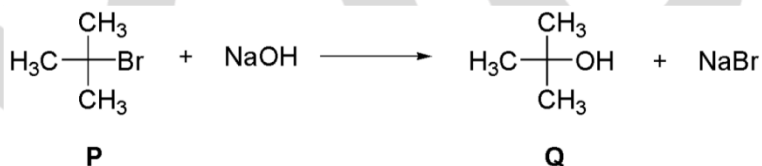
Here, $O_2(g)$ is paramagnetic due to two unpaired electrons present in π^* (antibonding orbitals)

(D) $x = C_6H_6(l) \rightarrow$ diamagnetic (incorrect)

It is due to presence of 0 unpaired electrons.

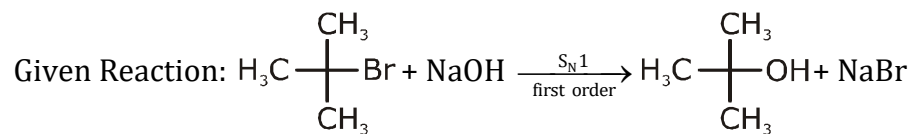
8. Which of the following plots is (are) correct for the given reaction?

($[P]_0$ is the initial concentration of P)



Answer: A

Solution:



At $t = 0$ P_0 0
 At $t = t$ P $P_0 - P$

We know,

$$\text{Rate} = k \left[\text{C(CH}_3)_2\text{Br} \right]$$

and, $\ln \frac{P_0}{P} = -kt$

here, $t_{1/2} = \frac{0.693}{k}$

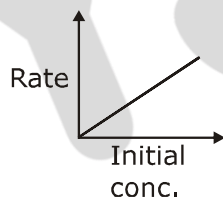
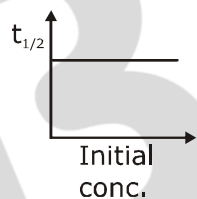
$$\ln \frac{P_0}{P} = -kt$$

$$\frac{[Q]}{[P_0]} = \frac{[P_0] - [P]}{[P_0]}$$

Solving, $\frac{[Q]}{[P_0]} = 1 - \frac{[P]}{[P_0]}$
 $= 1 - e^{-kt}$

As there is no inversion. Hence should be

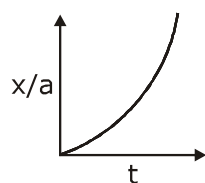
$\text{S}_{\text{N}}1 \rightarrow 1^{\text{st}}$ order



(C) $x = a\{1 - e^{-kt}\}$

$$x/a = 1 - e^{-kt}$$

$$\frac{x}{a} = \frac{Q}{P_0}$$



9. Which among the following statement(s) is(are) true for the extraction of aluminium from bauxite?
- (A) Hydrated Al_2O_3 precipitates, when CO_2 is bubbled through a solution of sodium aluminate.
- (B) Addition of Na_3AlF_6 lowers the melting point of alumina.
- (C) CO_2 is evolved at the anode during electrolysis.
- (D) The cathode is a steel vessel with a lining of carbon.

Answer: A, B, C, D

Solution:

Refer topic metallurgy

- (A) Extraction of aluminium (Hall's process and Hall Heroult's electrolytic cell):

The process involved in extraction of aluminium is Hall Heroult's process.

During process, Al_2O_3 is obtained as precipitate.

When CO_2 is bubbled through a solution of sodium aluminate.

The reaction is given as:

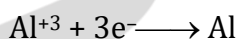


- (B) Electrolytic reduction of pure alumina takes place in steel box with lining of carbon (cathode) with cryolite (Na_3AlF_6) and fluorspar (CaF_2) which lowers the melting point and increases the conductivity of electrolyte.

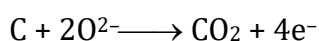
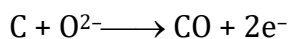
- (C) Electrolysis process in Hall's process:

Graphite rods acts as anode:

At cathode:



At anode: The oxygen liberated at anode reacts with the carbon of anode to produce CO and CO_2 .



- (D) Here the cathode is a steel vessel with a lining of carbon.

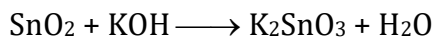
10. Choose the correct statement(s) among the following.

- (A) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is a reducing agent.
- (B) SnO_2 reacts with KOH to form $\text{K}_2[\text{Sn}(\text{OH})_6]$.
- (C) A solution of PbCl_2 in HCl contains Pb^{2+} and Cl^- ions.
- (D) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction.

Answer: A, B

Solution:

(A) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is a reducing agent since Sn^{2+} tends to convert into Sn^{4+}



or

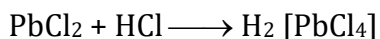


(B) First group cations (Pb^{2+}) form insoluble chloride with HCl that is PbCl_2 however it is slightly soluble in water and therefore lead +2 ion is never completely precipitated on adding hydrochloric acid in test sample of Pb^{2+} , rest of the Pb^{2+} ions are quantitatively precipitated with H_2S in acidic medium.

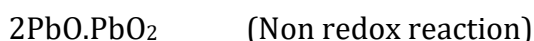
So that we can say that filtrate of first group contain solution of PbCl_2 in HCl which contains Pb^{2+} and Cl^- .

However in the presence of conc. HCl or excess HCl it can produce $\text{H}_2[\text{PbCl}_4]$.

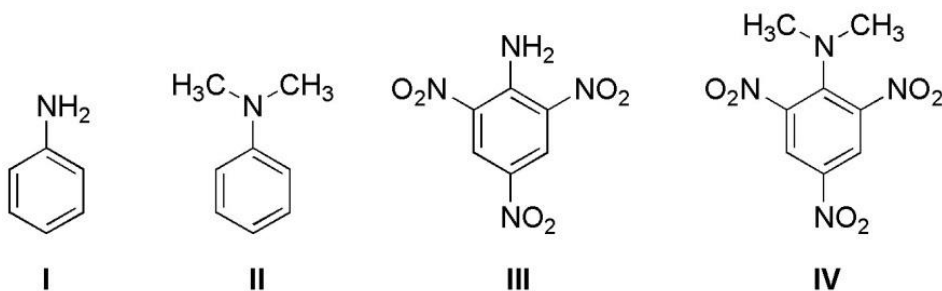
So, we can conclude A, B or A,B,C should be answers



or



11. Consider the following four compounds **I**, **II**, **III**, and **IV**.



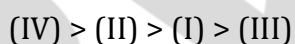
Choose the correct statement(s).

- (A) The order of basicity is **II** > **I** > **III** > **IV**.
- (B) The magnitude of pK_b difference between **I** and **II** is more than that between **III** and **IV**.
- (C) Resonance effect is more in **III** than in **IV**.
- (D) Steric effect makes compound **IV** more basic than **III**.

Answer: C, D

Solution:

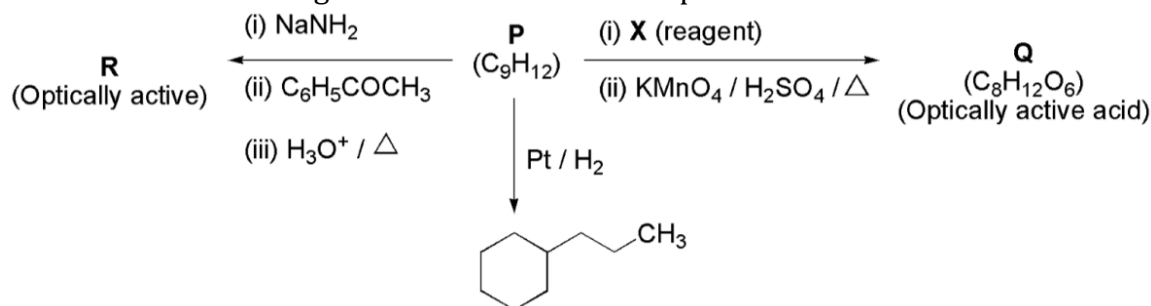
(A) Correct basic strength order of given compound is



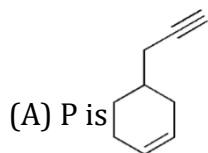
(B) Compound **IV** is a stronger base than **III** due to SIR effect, which basic strength difference between **I** & **II** is very less.

(C) In compound **IV** due to SIR (steric inhibition due to resonance) effect both $-NO_2$ and $-N(CH_3)_2$ group will be out of plane hence resonance effect in compound **IV** is less.

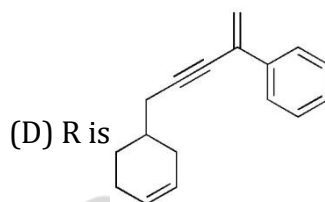
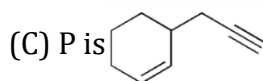
12. Consider the following transformations of a compound P.



Choose the correct option(s).

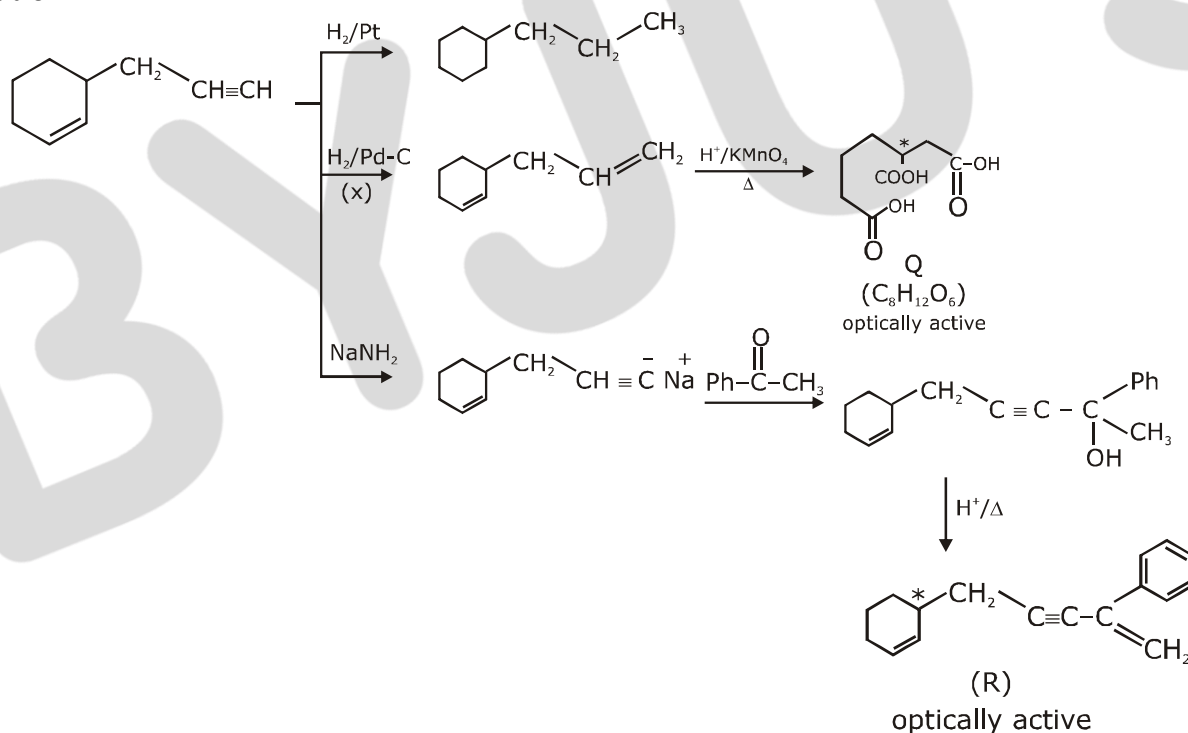


(B) X is Pd-C/quinoline/H₂



Answer: B, C

Solution:

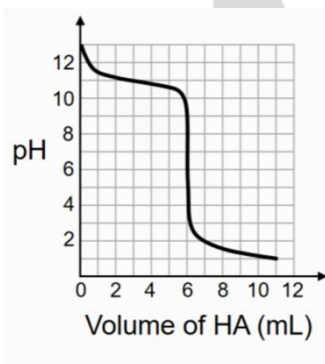


- NaNH₂ acts as a base for the double elimination of geminal or vicinal dihalides to give alkynes.
- Pd-C / quinoline + H₂ ⇒ a lindlar's catalyst that reduce only alkynes not alkenes.

SECTION 3 (Maximum Marks: 24)

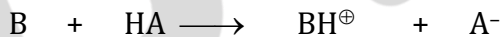
- This section contains **SIX (06)** questions. The answer to each question is a **NUMERICAL VALUE**.
- For Each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numerical keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:
Full Marks : +4 If ONLY the correct numerical value is entered;
Zero Marks : 0 In all other cases.

13. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$.



Answer: 3.3

Solution:



0.1M 0.1M

0mL

pH = 13

3mL \rightarrow 50% Neutralization

pH = 11

6 mL \rightarrow equivalence point

pH = 3 to 9

Equivalence point



0.1×6

0.1×6

= 0.6 m mol

= 0.6 m mol

0

0

0.6 m mol

Total volume = 12 ml

$$\text{Concentration of Salt} = \frac{0.6}{12}$$

$$\text{pH}=6 = \sqrt{\frac{k_w}{k_b} \times c} = \sqrt{\frac{10^{-14} \times 0.6}{k_b \times 12}} \quad \{\text{pH} = 0.6, [\text{H}^+] = 10^{-6}\}$$

$$\Rightarrow [\text{H}^+] = 10^{-6} = \sqrt{\frac{K_w \times 0.1 \times 6}{K_b \times 12}}$$

$$10^{-12} = \frac{10^{-14} \times 10^{-1}}{K_b} \times \frac{1}{2}$$

$$k_b = 5 \times 10^{-4}$$

$$\text{pk}_b = -\log k_b = -\log(5 \times 10^{-4}) = -\log 5 + 4\log 10$$

$$\text{pk}_b = 4 - 0.7$$

$$\text{pk}_b = 3.3$$

14. Liquids **A** and **B** form ideal solution for all compositions of **A** and **B** at 25°C. Two such solutions with 0.25 and 0.50 mole fractions of **A** have the total vapor pressures of 0.3 and 0.4 bar, respectively. What is the vapor pressure of pure liquid **B** in bar?

Answer: 0.2

Solution:

$$P_{\text{Total}} = 0.3 \quad \text{where } x_A = \frac{1}{4}$$

$$x_A + x_B = 1$$

$$\Rightarrow x_B = 0.75 = \frac{3}{4}$$

$$\Rightarrow 0.3 = \frac{1}{4} P_A^0 + \frac{3}{4} P_B^0 \quad \dots(1)$$

$$P_{\text{Total}} = 0.4 \quad \text{where } x_A = \frac{1}{2}, x_B = \frac{1}{2}$$

$$\Rightarrow 0.4 = \frac{1}{2} P_A^0 + \frac{1}{2} P_B^0 \quad \dots(2)$$

$$\text{eq.(1)} \times 2 - \text{eq.(2)}$$

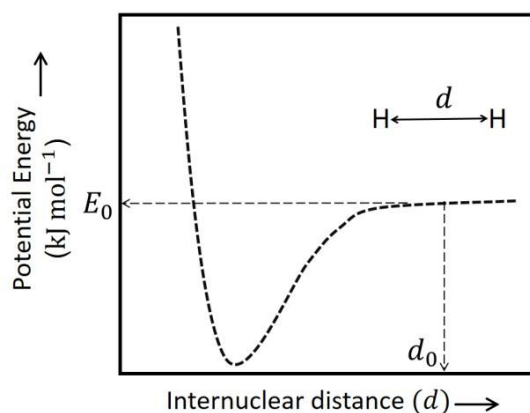
$$0.6 = \frac{1}{2} P_A^0 + \frac{3}{2} P_B^0$$

$$0.4 = \frac{1}{2} P_A^0 + \frac{1}{2} P_B^0$$

$$\begin{array}{r} - \quad - \quad - \\ \hline P_B^0 = 0.2 \text{ bar} \end{array}$$

15. The figure below is the plot of potential energy versus internuclear distance (d) of H_2 molecule in the electronic ground state. What is the value of the net potential energy E_0 (as indicated in the figure) in kJ mol^{-1} , for $d = d_0$ at which the electron-electron repulsion and the nucleus-nucleus repulsion energies are absent? As reference, the potential energy of H atom is taken as zero when its electron and the nucleus are infinitely far apart.

Use Avogadro constant as $6.023 \times 10^{23} \text{ mol}^{-1}$.



Answer: -5242.42

Solution:

P. E of 2 H-atoms

$$\text{Total eng} = \frac{\text{P.E}}{2}$$

\Rightarrow Potential Energy = 2 Total Energy

$$E = -13.6 \times \frac{z^2}{n^2} \text{ ev / atom}$$

$$= -2 \times 13.6 \times \frac{z^2}{n^2} \text{ ev/atom} + (-2 \times 13.6 \times \frac{z^2}{n^2}) \text{ ev/ atom}$$

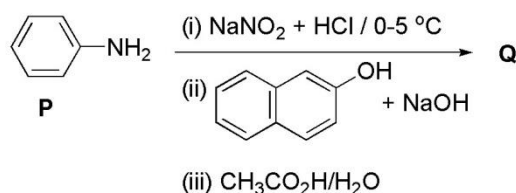
$$= -2 \times 2 \times 13.6 \times \frac{(1)^2}{(1)^2} \text{ eV/atom}$$

$$= -4 \times 13.6 \times 1.6 \times 10^{-19} \text{ J/atom} \times 6.023 \times 10^{23} \text{ atom/mole}$$

$$= -4 \times 13.6 \times 1.6 \times 6.023 \times 10^4 \text{ J/mole}$$

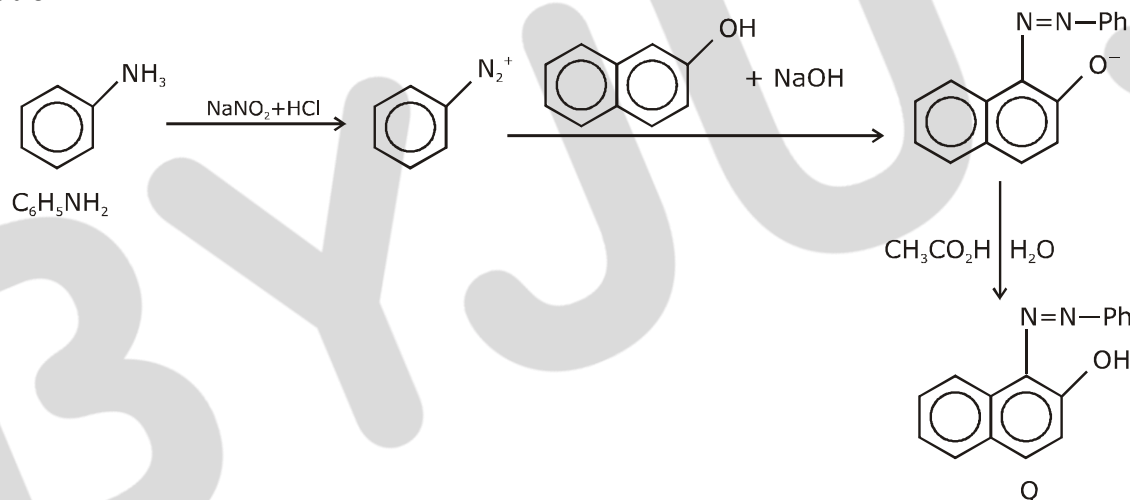
$$= -5242.42 \text{ KJ/mol}$$

16. Consider the reaction sequence from **P** to **Q** shown below. The overall yield of the major product **Q** from **P** is 75%. What is the amount in grams of **Q** obtained from 9.3 mL of **P**? (Use density of **P** = 1.00 g mL⁻¹; Molar mass of C = 12.0, H = 1.0, O = 16.0 and N = 14.0 g mol⁻¹)



Answer: 18.6

Solution:



Molecular weight of aniline (C₆H₅NH₂) = 77 + 14 + 2 = 93

Density of P = 1 gm ml⁻¹

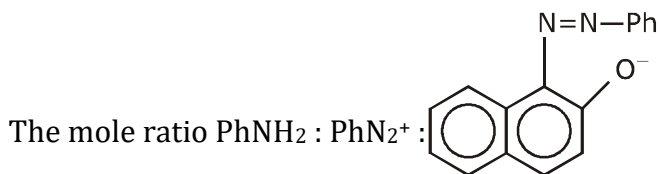
$$d = \frac{m}{v}$$

$$\Rightarrow m = d \times v$$

Mass of P = 9.3 × 1 = 9.3 g

9.3 ml of P = 9.3 gm

$$P = \frac{9.3}{93} = 0.1 \text{ mole of P}$$



$$= 1 : 1 : 1$$

So, the mole of Q formed will be 0.1 mole and extent of reaction is 100% but if it is 75% yield.

$$\text{Then amount of Q} = 0.1 \times \frac{75}{100} = 0.075 \text{ mol}$$

The molecular formula of Q = $\text{C}_{16}\text{H}_{12}\text{ON}_2$

$$\begin{aligned} \text{So, M. wt. of Q} &= 16 \times 12 + 12 \times 1 + 16 + 2 \times 14 \\ &= 192 + 12 + 16 + 28 \\ &= 248 \text{ gm / mol} \end{aligned}$$

$$\text{So, amount of Q} = 248 \times 0.075 = 18.6 \text{ gm}$$

17. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

$$\text{At } 298 \text{ K: } \Delta_f H^0(\text{SnO}_2(s)) = -581.0 \text{ kJ mol}^{-1}, \Delta_f H^0(\text{CO}_2(g)) = -394.0 \text{ kJ mol}^{-1},$$

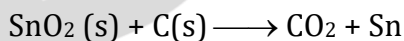
$$S^0(\text{SnO}_2(s)) = 56.0 \text{ J K}^{-1}\text{mol}^{-1}, S^0(\text{Sn}(s)) = 52.0 \text{ J K}^{-1}\text{mol}^{-1},$$

$$S^0(\text{C}(s)) = 6.0 \text{ J K}^{-1}\text{mol}^{-1}, S^0(\text{CO}_2(g)) = 210.0 \text{ J K}^{-1}\text{mol}^{-1}.$$

Assume that the enthalpies and the entropies are temperature independent.

Answer: 935

Solution:



$$\Delta H = (\Delta_f H)_P - (\Delta_f H)_R$$

$$= -394 + 581$$

$$= +187 \text{ KJ/mol}$$

$$\Delta S = (\Delta S)_P - (\Delta S)_R$$

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$$= 210 + 52 - 56 - 6$$

$$= 200 \text{ J/k mol}$$

$$\Delta G = 187 \times 1000 - 200 \times T$$

$$T = \frac{187 \times 1000}{200} = 935 \text{ K}$$

BYJU'S

18. An acidified solution of 0.05 M Zn^{2+} is saturated with $0.1 \text{ M H}_2\text{S}$. What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS ?

Use $K_{\text{sp}}(\text{ZnS}) = 1.25 \times 10^{-22}$ and overall dissociation constant of H_2S ,

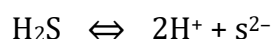
$$K_{\text{NET}} = K_1 K_2 = 1 \times 10^{-21}.$$

Answer: 0.2

Solution:

$$[\text{Zn}^{+2}] [\text{S}^{2-}] \leq K_{\text{sp}} (\text{ZnS})$$

$$[\text{S}^{2-}] \leq \frac{5}{4} \times \frac{10^{-22}}{0.05}$$



$$[\text{S}^{2-}] = \frac{K_{\text{net}} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

$$\frac{K_{\text{net}} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2} \leq \frac{5}{4} \times \frac{10^{-22}}{10^{-2} \times 5}$$

$$[\text{H}^+]^2 \geq \frac{10^{-21} \times 10^{-1} \times 4}{10^{-20}}$$

$$[\text{H}^+]^2 \geq 4 \times 10^{-2}$$

$$[\text{H}^+] \geq 2 \times 10^{-1} = 0.2$$

Alternate:

$$[\text{Zn}^{+2}] [\text{S}^{2-}] \leq K_{\text{sp}}$$

$$[\text{S}^{2-}] \leq \frac{5}{4} \times \frac{10^{-22}}{0.05} = \frac{1}{4} \times 10^{-20}$$



$$[\text{H}^+]^2 = \frac{K_1 K_2 \times [\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{10^{-21} \times 0.1}{[\text{S}^{2-}]}$$

$$[\text{S}^{2-}] = \frac{10^{-22}}{[\text{H}^+]^2} \leq \frac{1}{4} \times 10^{-20}$$

$$[\text{H}^+]^2 \geq 4 \times 10^{-2}$$

$$[\text{H}^+] \geq 0.2$$