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.

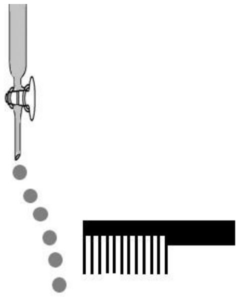
Hence, atomic number can be = 11

That is = (n + 2) = 11

n = 9

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

2. Consider the following compounds in the liquid form:
O_2, HF, H_2O, NH_3, H_2O_2, CCl_4, $CHCl_3$, C_6H_6, C_6H_5Cl.
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, H_2O, NH_3, H_2O_2, $CHCl_3$, C_6H_5Cl

Non-polar molecules: O_2, CCl_4, Benzene

3. In the chemical reaction between stoichiometric quantities of $KMnO_4$ and KI in weakly basic solution, what is the number of moles of I_2 released for 4 moles of $KMnO_4$ consumed?

Answer: 6

Solution:

Chemical reaction of $KMnO_4$ and KI in weakly basic solution is given as

$KMnO_4 + KI \xrightarrow[\text{Basic}]{\text{weak}} MnO_2 + I_2$

$KMnO_4 \longrightarrow MnO_2$

Oxidation state of Mn $+7$ $+4$

So n-factor of $KMnO_4 = 3$

$2I^- \longrightarrow I_2$

n-factor of I_2 is = 2

$KMnO_4 \quad + \quad KI \longrightarrow \quad MnO_4 \quad + \quad I_2$

n-factor = 3 n-factor = 2

Equivalents of $KMnO_4$= Equivalents of I_2

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

$3 \times$ moles of $KMnO_4 = 2 \times$ moles of I_2

$3 \times 4 = 2 \times$ moles of I_2

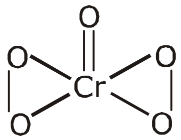
Moles of I_2 = 6 moles

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

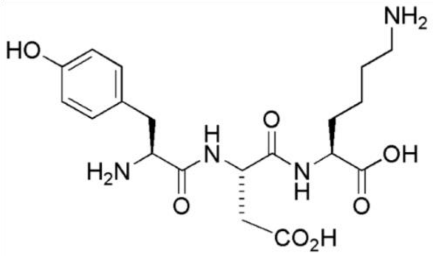
Solution:

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.



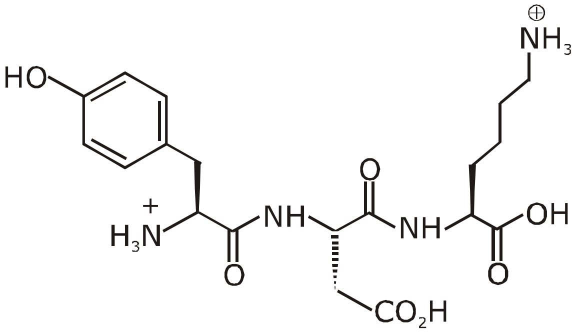
If the absolute values of the net charge of the peptide at pH = 2, pH = 6, and pH = 11 are $|z_1|$, $|z_2|$, and $|z_3|$, respectively, then what is $|z_1| + |z_2| + |z_3|$?

Answer: 5

Solution:

(i) At pH = 2 (Highly acidic)

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

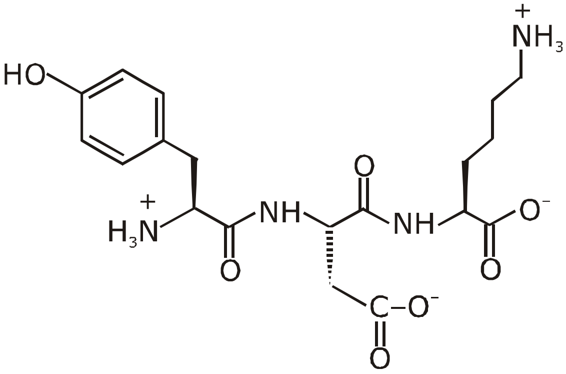


Net charge +2

|Z1| = 2 at pH = 2

(ii) At pH = 6 (neutral solution)

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

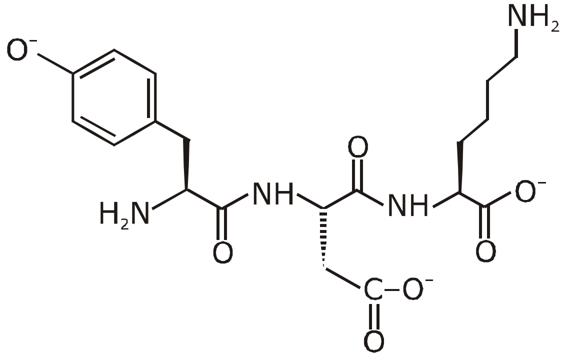


net charge = 0

|Z2| = 0 at pH = 6

(iii) At pH = 11 (basic medium)

In basic medium the given tripeptide exist in anionic form.



Net charge = –3

|Z3| = 3

Therefore |Z1| + |Z2| + |Z3| = 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:

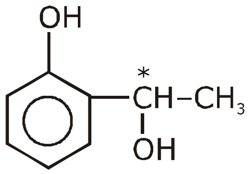
DBE (Double bond equivalent) of $C_8H_{10}O_2$ is

= Number of carbon atoms – (Number of monovalent atoms)/2 + 1

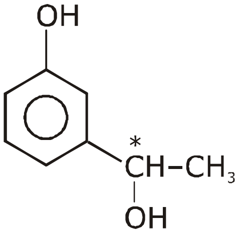
= 8 – 10/2 + 1 = 4

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

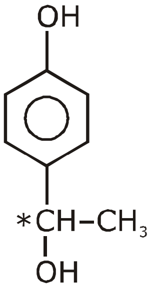
Note: C* represent chiral carbon. So it will have (d and l) optically active isomers.



(d + l)



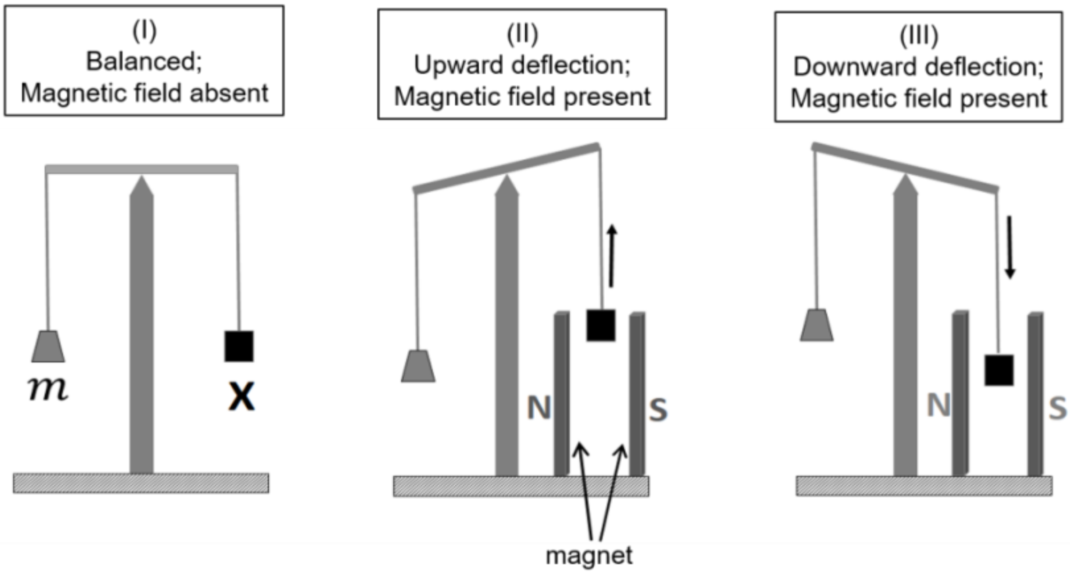
(d + l)



(d + l)

Total optically active isomer = 6

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 $H_2O(l)$, deflection of the panis upwards.

(B) If **X** is $K_4[Fe(CN)_6](s)$, deflection of the panis upwards.

(C) If **X** is $O_2\,(g)$, deflection of the panis downwards.

(D) If **X** is $C_6H_6(l)$, deflection of the panis 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.

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

(C) $x = O_2 \rightarrow$ Paramagnetic

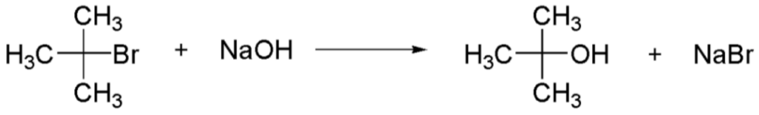
Here, $O_2(g)$ is paramagnetic due to two unpaired electrons present in π^* (antibonding orbitals)

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

It is due to presence of 0 unpaired electrons.

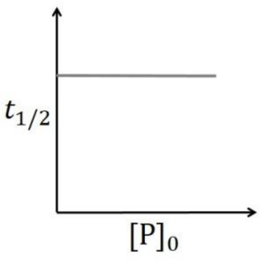
8. Which of the following plots is (are) correct for the given reaction?

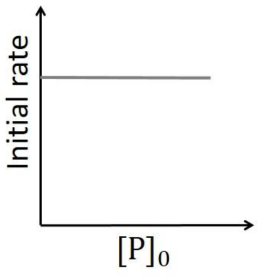
([P]$_0$ is the initial concentration of **P**)

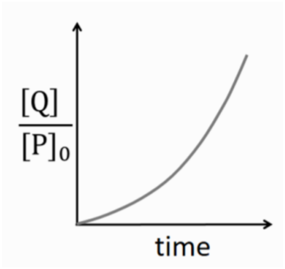


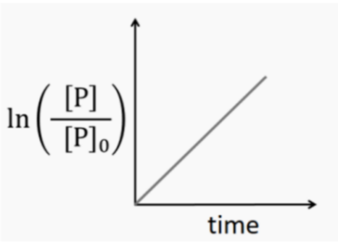
$$(CH_3)_3C{-}Br + NaOH \longrightarrow (CH_3)_3C{-}OH + NaBr$$

P **Q**

(A)


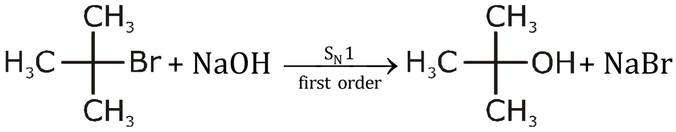
(B)


(C)


(D)


Answer: A

Solution:

Given Reaction: 

$$(CH_3)_3C{-}Br + NaOH \xrightarrow[\text{first order}]{S_N1} (CH_3)_3C{-}OH + NaBr$$

At t = 0 P_o 0

At t = t P $P_o - P$

We know,

Rate = k[]

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

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

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

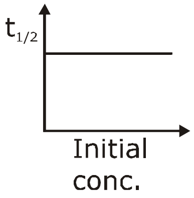
$$\frac{[Q]}{[P_o]} = \frac{[P_o]-[P]}{[P_o]}$$

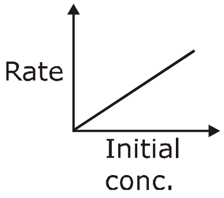
Solving, $\frac{[Q]}{[P_o]} = 1 - \frac{[P]}{[P_o]}$

$= 1 - e^{-kt}$

As there is no inversion. Hence should be

$S_N1 \rightarrow 1^{st}$ order

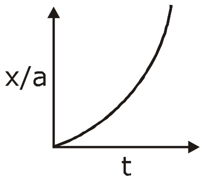




(C) $x = a\{1 - e^{-kt}\}$

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

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



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_3 is bubbled through a solution of sodium aluminate.

The reaction is given as:

$2Na[Al(OH)_4](aq.) + CO_2 \longrightarrow Na_2CO_3 + H_2O + 2Al(OH)_3 (\downarrow)$ or $Al_2O_3.2H_2O$ (ppt)

(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:

$Al^{+3} + 3e^- \longrightarrow Al$

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

$C + O^{2-} \longrightarrow CO + 2e^-$

$C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

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

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

(A) $SnCl_2.2H_2O$ is a reducing agent.

(B) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$.

(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) $SnCl_2.2H_2O$ is a reducing agent since Sn^{2+} tends to convert into Sn^{4+}

$SnO_2 + KOH \longrightarrow K_2SnO_3 + H_2O$

or

Amphoteric $K_2[Sn(OH)_6]$

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

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 $H_2[PbCl_4]$.

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

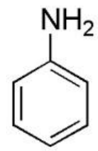
$PbCl_2 + HCl \longrightarrow H_2 [PbCl_4]$

$Pb_3O_4 + HNO_3 \longrightarrow PbO_2 + Pb(NO_3)_2 + H_2O$

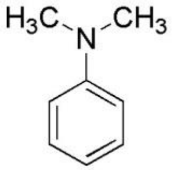
or

$2PbO.PbO_2$ (Non redox reaction)

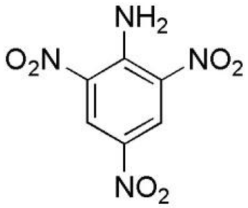
11. Consider the following four compounds **I**, **II**, **III**, and **IV**.



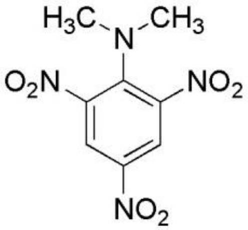
I



II



III



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:

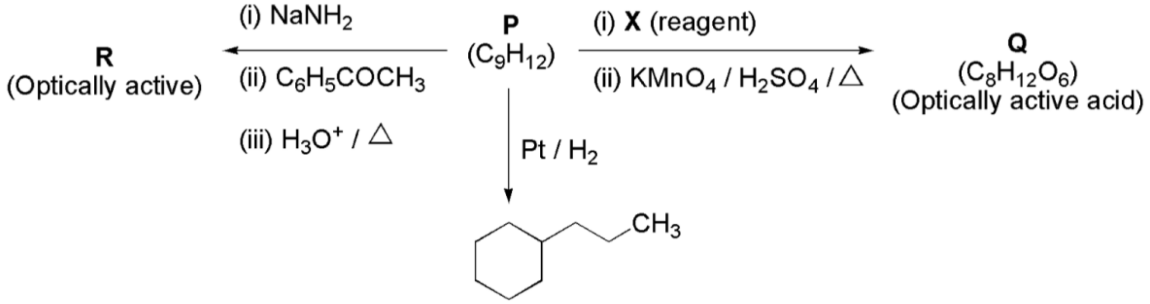
(A) Correct basic strength order of given compound is

(IV) > (II) > (I) > (III)

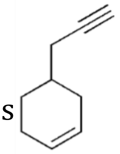
(B) Compound IV is a stronger base than III due to SIR effect, which basic strength difference between I & II is very less.

(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.

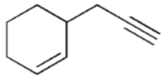
12. Consider the following transformations of a compound **P**.

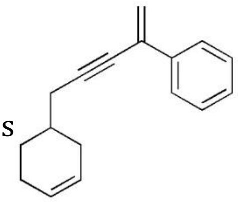


Choose the correct option(s).

(A) P is 

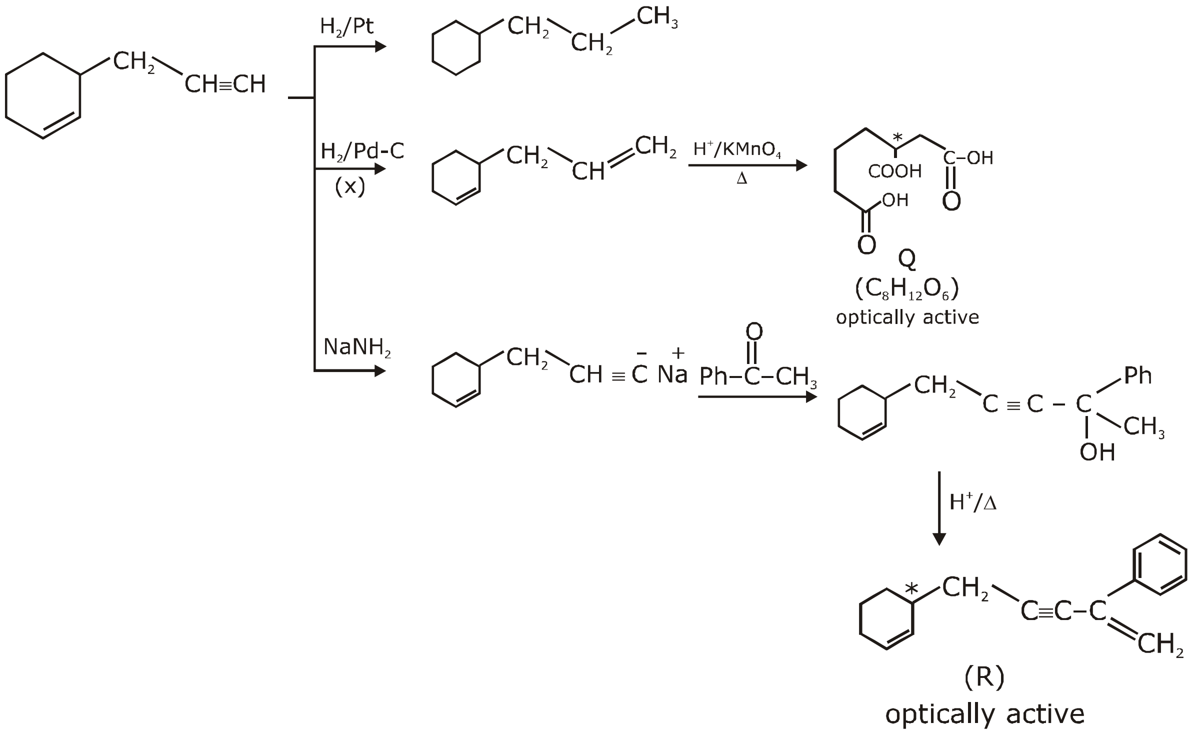
(B) X is Pd-C/quinoline/H$_2$

(C) P is 

(D) R is 

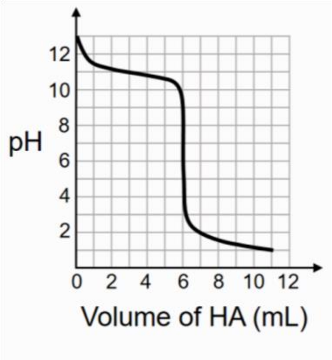
Answer: B, C

Solution:



- NaNH$_2$ acts as a base for the double elimination of geminal or vicinal dihalides to give alkynes.
- Pd-C / quinoline + H$_2$⇒ a lindlar's catalyst that reduce only alkynes not alkenes.

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:

$B \quad + \quad HA \longrightarrow \quad BH^{\oplus} \quad + \quad A^-$

0.1M 0.1M

0mL pH = 13

3mL → 50% Neutralization pH = 11

6 mL → equivalence point pH = 3 to 9

Equivalence point

$B \quad + \quad HA \quad \longrightarrow \quad BH^+ + \quad A^-$

0.1×6 $\quad$ 0.1×6

= 0.6 m mol $\quad$ = 0.6 m mol

0 $\quad$ 0 $\quad$ 0.6 m mol

Total volume = 12 ml

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

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

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

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

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

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

$pk_b = 4 - 0.7$

$pk_b = 3.3$

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:

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

$x_A + x_B = 1$

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

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

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

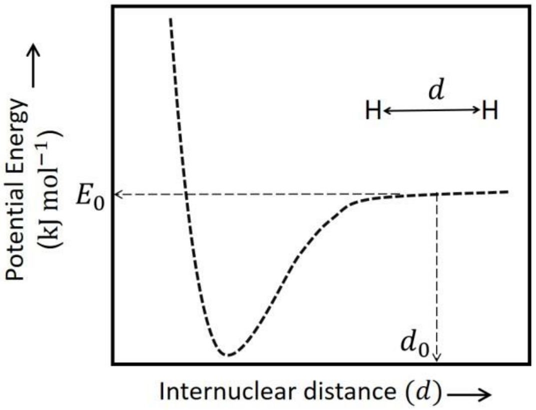
$\Rightarrow \quad 0.4= \frac{1}{2} P_A^0 + \frac{1}{2} P_B^0 \qquad ...(2)$

eq.(1) × 2 – eq.(2)

$$\begin{array}{l} 0.6 = \frac{1}{2} P_A^0 + \frac{3}{2} P_B^0 \\ 0.4= \frac{1}{2} P_A^0 + \frac{1}{2} P_B^0 \\ - \quad - \qquad - \\ \hline P_B^0 = 0.2 \text{ bar} \end{array}$$

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 6.023×10^{23} mol^{-1}.



Answer: –5242.42

Solution:

P. E of 2 H-atoms

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

⇒Potential Energy = 2 Total Energy

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

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

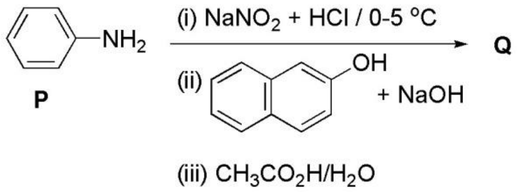
$= -2\times 2\times 13.6\times \frac{(1)^2}{(1)^2}$ ev/atom

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

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

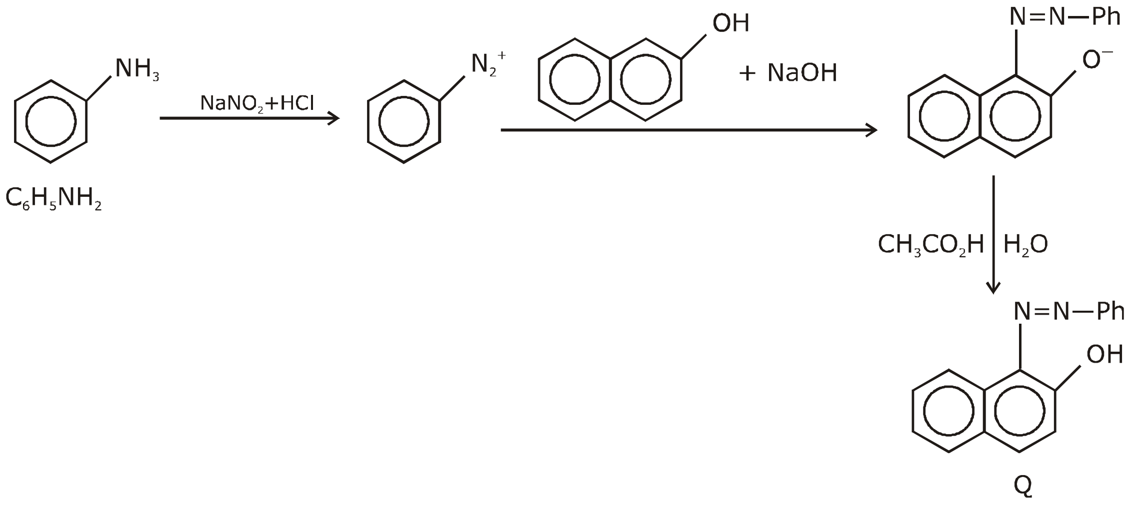
$= -5242.42$ KJ/mol

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 ($C_6H_5NH_2$) = 77 + 14 + 2 = 93

Density of P = 1 gm ml^{-1}

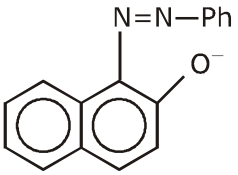
$d = \frac{m}{v}$

$\Rightarrow m = d \times v$

Mass of P = 9.3 × 1 = 9.3 g

9.3 ml of P = 9.3 gm

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

The mole ratio $PhNH_2 : PhN_2^+$: 

= 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.

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

The molecular formula of Q = $C_{16}H_{12}ON_2$

So, M. wt. of Q = 16 × 12 + 12 × 1 + 16 + 2 × 14

= 192 + 12 + 16 + 28

= 248 gm / mol

So, amount of Q = 248 × 0.075= 18.6 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.

At 298 K: $\Delta_f H^0(SnO_2(s)) = -581.0$ kJ mol^{-1}, $\Delta_f H^0(CO_2(g)) = -394.0$ kJ mol^{-1},

$S^0(SnO_2(s)) = 56.0$J K^{-1}mol^{-1}, $S^0(Sn(s)) = 52.0$ J K^{-1}mol^{-1},

$S^0(C(s)) = 6.0$J K^{-1}mol^{-1}, $S^0(CO_2(g)) = 210.0$ J K^{-1}mol^{-1}.

Assume that the enthalpies and the entropies are temperature independent.

Answer: 935

Solution:

$SnO_2 (s) + C(s) \longrightarrow CO_2 + Sn$

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

$= -394 + 581$

$= +187$ KJ/mol

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

$= 210 + 52 - 56 - 6$

$= 200$ J/k mol

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

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

18. An acidified solution of 0.05 MZn^{2+} is saturated with 0.1 M H_2S. What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS?

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

$K_{NET} = K_1K_2 = 1 \times 10^{-21}$.

Answer: 0.2

Solution:

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

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

$H_2S \Leftrightarrow 2H^+ + s^{2-}$

$$[S^{2-}] = \frac{K_{net} \times [H_2S]}{[H^+]^2}$$

$$\frac{K_{net} \times [H_2S]}{[H^+]^2} \leq \frac{5}{4} \times \frac{10^{-22}}{10^{-2} \times 5}$$

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

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

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

Alternate:

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

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

$H_2S \Leftrightarrow 2H^+ + S^{2-}$

$$[H^+]^2 = \frac{K_1K_2 \times [H_2S]}{[S^{2-}]} = \frac{10^{-21} \times 0.1}{[S^{2-}]}$$

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

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

$[H^+] \geq 0.2$