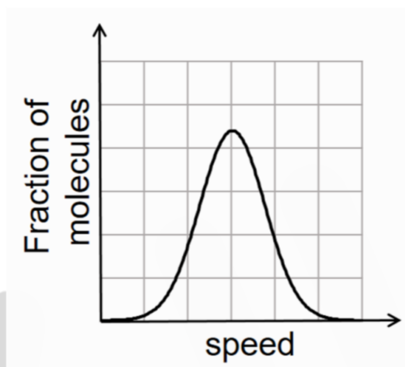
SECTION 1 (Maximum Marks: 18)

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options is 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 questions is unanswered);
Negative Marks : –1 In all other cases.

1. If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average, and the root mean square speeds, respectively, is



(A) 1 :1 : 1
(B) 1 :1 : 1.224
(C) 1 :1.128 : 1.224
(D) 1 :1.128 : 1

Answer:C

Solution:

Graph represents symmetrical distribution of speed and hence, the most probable and the average speed should be same. But the root mean square speed must be greater than the average speed.

According to distribution of molecular speed curve,

$$u_{mps} = \sqrt{\frac{2RT}{mol.wt.}}$$

$$u_{avg} = \sqrt{\frac{8RT}{\pi mol.wt.}}$$

$$u_{rms} = \sqrt{\frac{3RT}{mol.wt.}}$$

$$u_{mps} : u_{avg} : u_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$
$$= 1 : 1.128 : 1.224$$

2. Which of the following liberates O_2 upon hydrolysis?

(A) Pb_3O_4

(B) KO_2

(C) Na_2O_2

(D) Li_2O_2

Answer: B

Solution:

(A) $Pb_3O_4 + H_2O \longrightarrow$ No reaction (due to insoluble in water)

(B) Superoxides liberate oxygen with water.

$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2\uparrow$

(C) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

(D) $Li_2O_2 + 2H_2O \longrightarrow 2LiOH + H_2O_2$

3. A colorless aqueous solution contains nitrates of two metals, **X** and **Y**. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue **P** and a solution **Q**. The residue **P** was soluble in aq. NH_3 and also inexcess sodium thiosulfate. The hot solution **Q** gave a yellow precipitate with KI. The metals **X** and **Y**, respectively, are

(A) Ag and Pb

(B) Ag and Cd

(C) Cd and Pb

(D) Cd and Zn

Answer: A

Solution:

x = Ag ; y = Pb ; P = AgCl ; Q = $PbCl_2$

(1) $\underset{(x)}{AgNO_3} + NaCl \longrightarrow \underset{(P)}{AgCl\downarrow} + NaNO_3$

(2) $AgCl(s)\downarrow + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ Cl^-$

(P) (soluble complex)

(3) $AgCl + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)] + NaCl$

(residue-p) (excess) (soluble complex)

(4) $Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2\downarrow + 2NaNO_3$

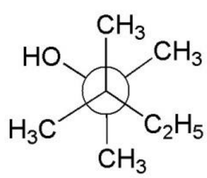
(y) whiteppt(Q) (soluble in hot water)

(5) $PbCl_2 + 2KI \longrightarrow PbI_2 + 2KCl$

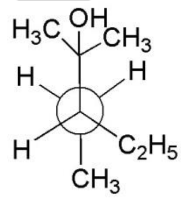
(hot solution) yellow ppt

Q

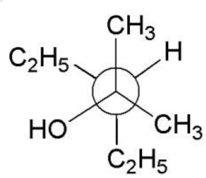
4. Newman projections **P**, **Q**, **R** and **S** are shown below:



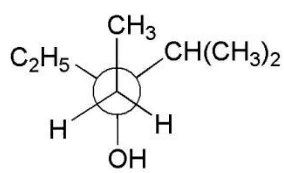
P



Q



R



S

Which one of the following options represents identical molecules?

(A) **P** and **Q**

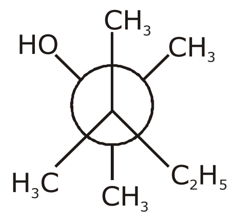
(B) **Q** and **S**

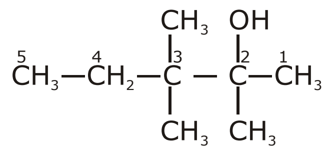
(C) **Q** and **R**

(D) **R** and **S**

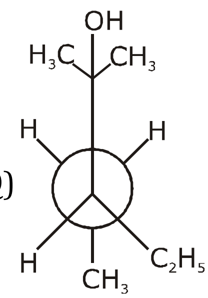
Answer: C

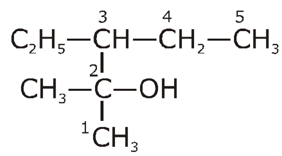
Solution:

(P)


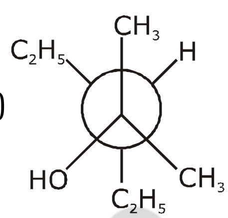


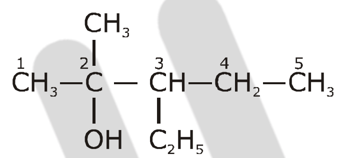
2,3,3-trimethyl Pentan-2-ol

(Q)


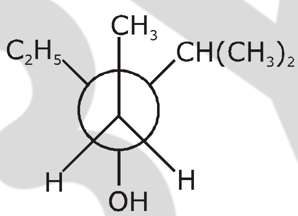


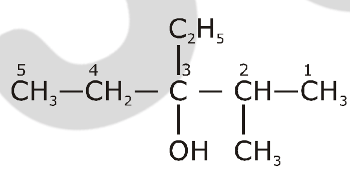
3-Ethyl-2-methyl Pentan-2-ol

(R)




3-Ethyl-2-methyl Pentan-2-ol

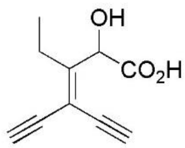
(S)


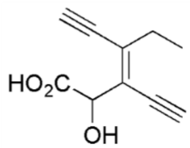


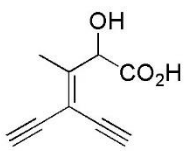
3-Ethyl-2-methyl Pentan-3-ol

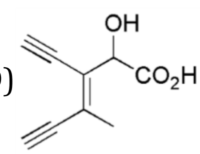
Q and R are identical molecules.

5. Which one of the following structures has the IUPAC name 3-ethynyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid?

(A) 

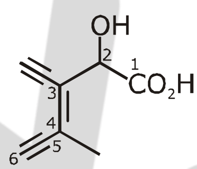
(B) 

(C) 

(D) 

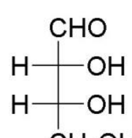
Answer: D

Solution:



3-ethynyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid

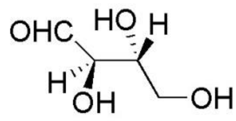
6. The Fischer projection of D-erythrose is shown below.

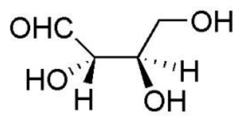


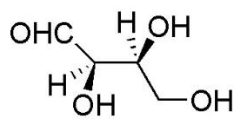
D-Erythrose

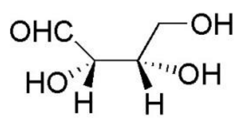
D-Erythrose and its isomers are listed as **P**, **Q**, **R**, and **S** in **Column-I**. Choose the correct relationship of **P**, **Q**, **R**, and **S** with D-erythrose from **Column II**.

Column-I

P. 

Q. 

R. 

S. 

Column-II

1. Diastereomer
2. Identical
3. Enantiomer

(A) **P**→2, **Q**→3, **R**→2, **S**→2

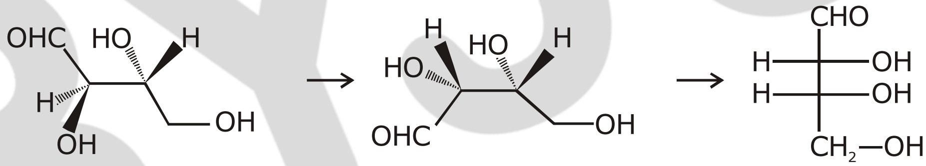
(B) **P**→3, **Q**→1, **R**→1, **S**→2

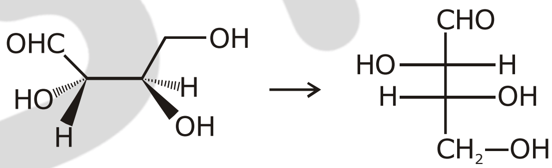
(C) **P**→2, **Q**→1, **R**→1, **S**→3

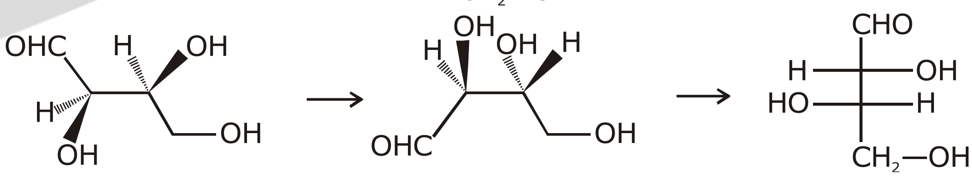
(D) **P**→2, **Q**→3, **R**→3, **S**→1

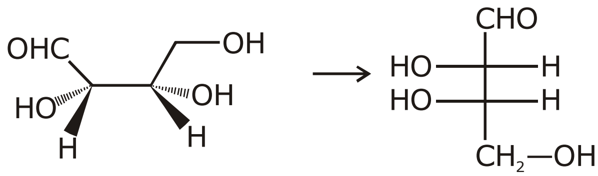
Answer: C

Solution:

P. 

Q. 

R. 

S. 

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 corresponding to the correct answer.
- 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;

PartialMarks : +3 If all four options is 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;

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 thermodynamics, the $P - V$ work done is given by

$$w = -\int dV P_{ext}$$

For a system undergoing a particular process, the work done is,

$$w = -\int dV\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)$$

This equation is applicable to a

(A) System that satisfies the van der Waals equation of state.

(B) Process that is reversible and isothermal.

(C) Process that is reversible and adiabatic.

(D) Process that is irreversible and at constant pressure.

Answer: A, B, C

Solution:

$$w = -\int P_{ext.} dV$$

From van der waal equation of state for one mole gas.

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

$$P=\left[\frac{RT}{V-b}-\frac{a}{V^2}\right]$$

For reversible process

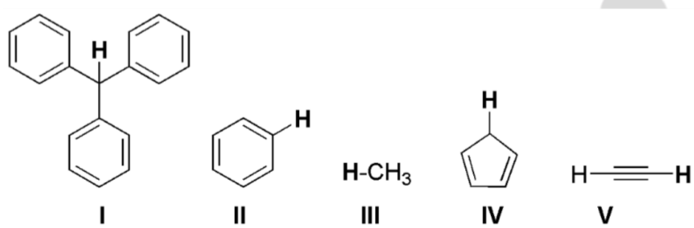
$P_{ext.} = P_{gas}$

$$W=-\int\left(\frac{RT}{v-b}-\frac{a}{v^2}\right)dv$$

So, process is not applicable only for irreversible process.

Hence Ans. A,B,C

8. With respect to the compounds **I-V**, choose the correct statement(s).



(A) The acidity of compound **I** is due to delocalization in the conjugate base.

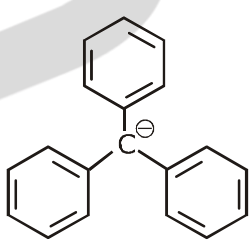
(B) The conjugate base of compound **IV** is aromatic.

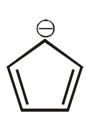
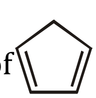
(C) Compound **II** becomes more acidic, when it has a -NO_2 substituent.

(D) The acidity of compounds follows the order **I >IV>V>II>III**.

Answer: A, B, C

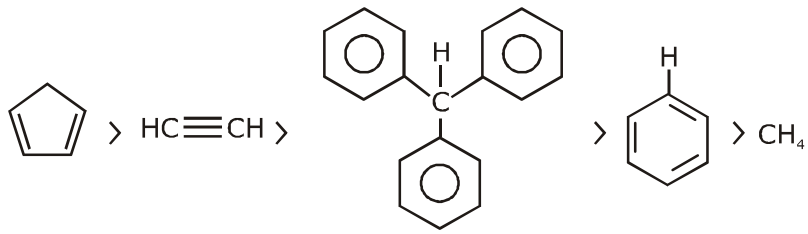
Solution:

(A)  is a conjugate base of compound I Which is stabilized by delocalisation or resonance.

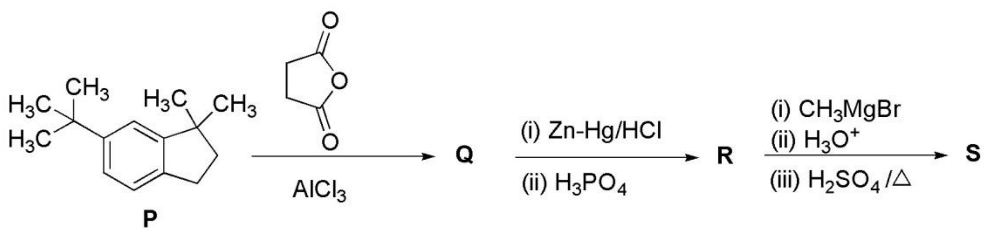
(B)  is a conjugate base of , which is an aromatic compound.

(C) –NO_2 group is strong electron withdrawing group, which increases acidic strength of compound II.

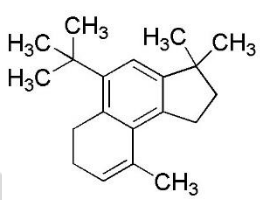
(D) The order of acidic strength.



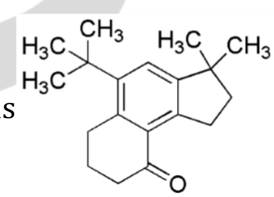
9. In the reaction scheme shown below, **Q**, **R**, and **S** are the major products.

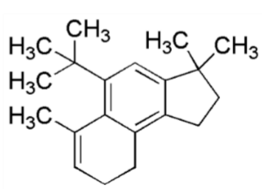


The correct structure of

(A) **S** is 

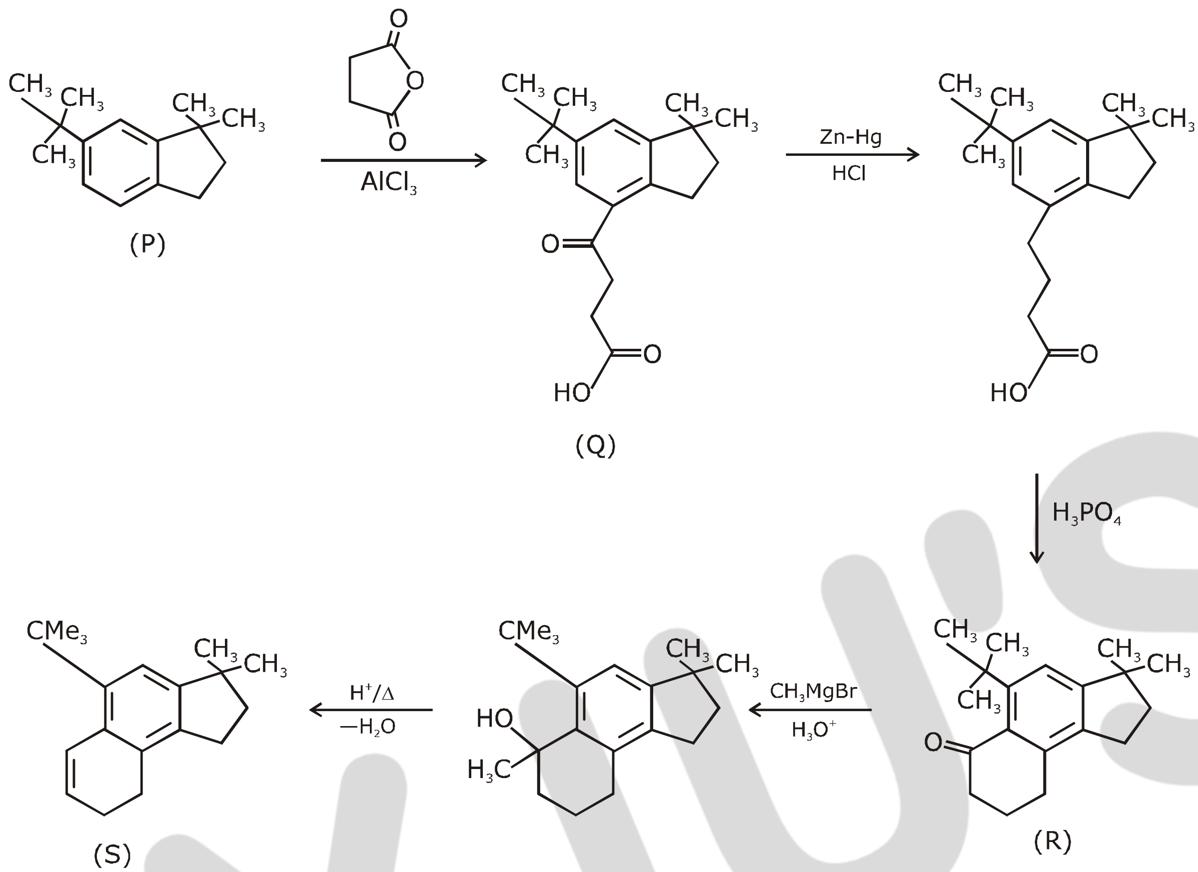
(B) **Q** is 

(C) **R** is 

(D) **S** is 

Answer: B, D

Solution:



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

(A) $[FeCl_4]^-$ has tetrahedral geometry.

(B) $[Co(en)(NH_3)_2Cl_2]^+$has 2 geometrical isomers.

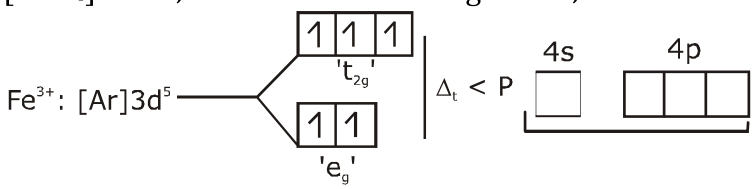
(C) $[FeCl_4]^-$ has higher spin-only magnetic moment than $[Co(en)(NH_3)_2Cl_2]^+$.

(D) The cobalt ion in $[Co(en)(NH_3)_2Cl_2]^+$ has sp^3d^2 hybridization.

Answer: A, C

Solution:

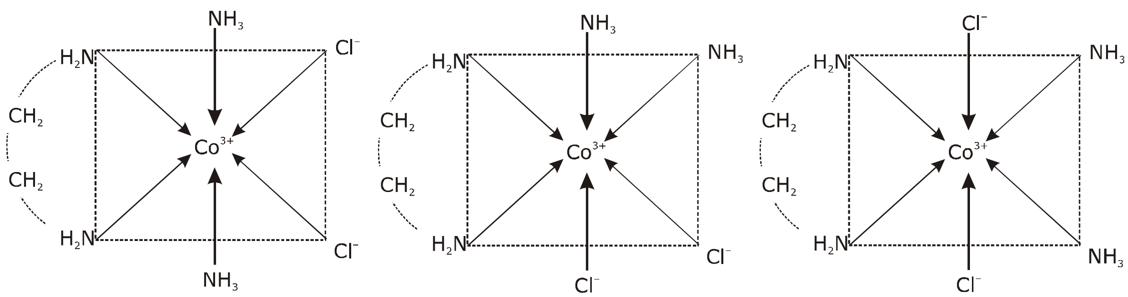
(A) $[FeCl_4]^-$; $Cl^-$is weak field ligand So, it cannot be paired (unpaired electrons)



sp^3– hybridization

$[FeCl_4]^-$ is sp^3 hybridized and has tetrahedral geometry with number of unpaired electrons (n) = 5

(B) $[CO(en)(NH_3)_2Cl_2]^+$ has three geometrical isomers.

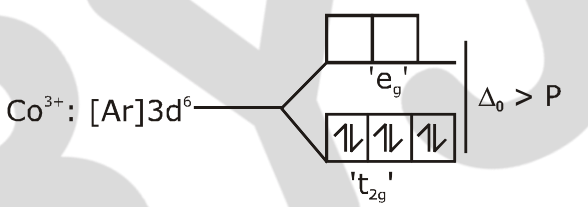


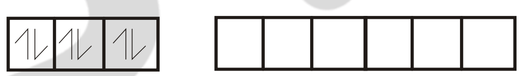
(C) Number of unpaired electron (n)= 5

So, spin-only magnetic moment $\mu_{(s)} = \sqrt{n(n+2)}$

$$\mu_{(s)} = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{B.M.}$$

(D) $[CO(en)(NH_3)_2Cl_2]^+$; NH_3, en are strong field ligand so all unpaired electrons get paired.





d^2sp^3 hybridization (octahedral geometry)

Number of unpaired electron (n) = 0

Spin-only magnetic moment = $\mu_{(s)} = \sqrt{n(n+2)} = 0$

11. With respect to hypochlorite, chlorate and perchlorate ions, choose the correct statement(s).

(A) The hypochlorite ion is the strongest conjugate base.

(B) The molecular shape of only chlorate ion is influenced by the lone pair of electrons of Cl.

(C) The hypochlorite and chlorate ions disproportionate to give rise to identical set of ions.

(D) The hypochlorite ion oxidizes the sulfite ion.

Answer: A, B, D

Solution:

Hypochlorite ion $\rightarrow ClO^-$

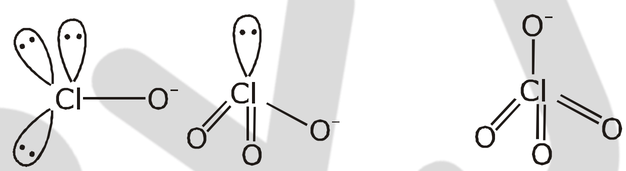
Chlorate ion $\rightarrow ClO_3^-$

Perchlorate ion $\rightarrow ClO_4^-$

Acidic nature $\rightarrow HClO < HClO_3 < HClO_4$

Conjugate Base order $\rightarrow ClO^- > ClO_3^- > ClO_4^-$

(B)



sp^3 (Linear) Sp^3 (pyramidal) Sp^3 (tetrahedral)

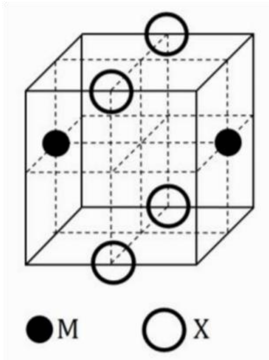
In chlorate ion bond angle changes due to presence of lone pair on chlorine atom while hypochlorite ion is linear and perchlorate ion is tetrahedral and there is no effect of lone pair on hypochlorite ion.

(C) $\overset{(+1)}{3OCl^-} \xrightarrow{\text{hot}} \overset{(-1)}{2Cl^-} + \overset{(+5)}{ClO_3^-}$

$\overset{(+5)}{4ClO_3^-} \xrightarrow[\text{lower temperature}]{\text{absence of catalyst}} \overset{+7}{3ClO_4^-} + \overset{(-1)}{Cl^-}$

(D) $ClO^- + SO_3^- \longrightarrow Cl^- + SO_4^{2-}$

12. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s).



(A) The empirical formula of the compound is MX.
(B) The cation M and anion X have different coordination geometries.
(C) The ratio of M-X bond length to the cubic unit cell edge length is 0.866.
(D) The ratio of the ionic radii of cation M to anion X is 0.414.

Answer: A, C

Solution:

According to the given diagram, structure seems to be B.C.C.

(1) Empirical formula $\rightarrow$ MX

(2) C. No. of 'M' ion = 8 [same co-ordination Geometry]
C. No. of 'X' ion = 8 [same co-ordination Geometry]

(3) $\text{M–X Bond Length} = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{\sqrt{2}}\right)^2}$

$\text{M–X Bond Length} = a\sqrt{\frac{1}{4}+\frac{1}{2}}$

$$\frac{\text{M}-\text{X bond length}}{\text{a(edge length)}} = \frac{\sqrt{3}}{2} = 0.866$$

(4) As it is B.C.C.

$$r_{X^-} + r_{M^+} = \sqrt{\frac{3}{2}}a$$

$$0.732 \le \frac{r_{M^+}}{r_{X^-}} < 1$$

Ans. A,C

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. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution?

Exp. No.	Vol. of NaOH (mL)
1	12.5
2	10.5
3	9.0
4	9.0
5	9.0

Answer: 0.11

Solution:

$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$

5ml M

0.1 M

By law of equivalence

Number of eq. of NaOH = Number of eq. of oxalic acid

M = [NaOH] = $\dfrac{[H_2C_2O_4] \times \text{vol.} \times 2}{\text{vol. of NaOH}}$

$[NaOH]_1 = \dfrac{5 \times 0.1 \times 2}{12.5} = \dfrac{1}{12.5}$

$[NaOH]_2 = \dfrac{5 \times 0.1 \times 2}{10.5} = \dfrac{1}{10.5}$

$[NaOH]_3 = \dfrac{5 \times 0.1 \times 2}{9} = \dfrac{1}{9} = [NaOH]_4 = [NaOH]_5$

$$[NaOH]\text{ Final Result } = \frac{\frac{1}{12.5} + \frac{1}{10.5} + \frac{1}{9} \times 3}{5}$$

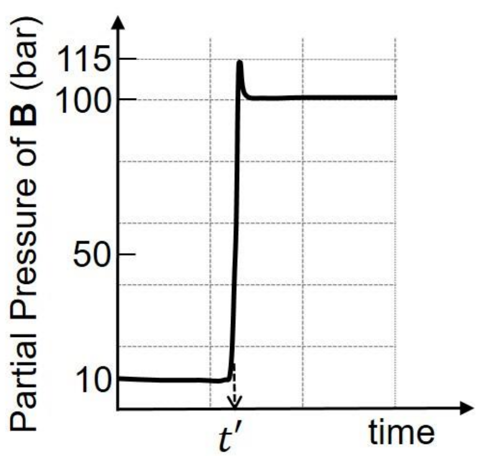
$$= \frac{\left[\frac{2}{25} + \frac{2}{21} + \frac{1}{3}\right]}{5}$$

$$= \frac{0.08 + 0.095 + 0.333}{5}$$

$$= 0.102 \simeq 0.11 \text{ Ans.}$$

14. Consider the reaction A ⇌ B at 1000 K. At time t', the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment, the partial pressure of **A** was maintained at 1 bar. Given below is the plot of the partial pressure of **B** with time.

What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K?



Answer: 0.25

Solution:

$K_{eq.} = \frac{[P_B]}{[P_A]}$; $\{[P_A] = 1\,atm\}$

$K_{eq.\,2000\,K} = 100$

$K_{eq.\,1000\,K} = 10$

$$\frac{\Delta G^0_{1000K}}{\Delta G^0_{2000K}} = \frac{(-RT\ln k_{eq})_{1000K}}{(-RT\ln k_{eq})_{2000K}} = \frac{1000\times \ln 10}{2000\times \ln 100} = \frac{1}{4} = 0.25$$

Ans. = 0.25

15. Consider a 70% efficient hydrogen-oxygen fuel cell working under standard conditions at 1 bar and 298 K. Its cell reaction is

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

The work derived from the cell on the consumption of 1.0×10^{-3} mol of $H_2(g)$ is used to compress 1.00 mol of a monoatomic ideal gas in a thermally insulated container. What is the change in the temperature (in K) of the ideal gas?
The standard reduction potentials for the two half-cells are given below.

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2\,H_2O\,(l),\quad E^0 = 1.23\text{ V},$$
$$2H^+(aq) + 2e^- \rightarrow H_2\,(g),\quad E^0 = 0.00\text{ V}$$

Use $F = 96500$ C mol^{-1}, R = 8.314 J mol^{-1} K^{-1}.

Answer: 13.32

Solution:

E^0_{cell} = 1.23 volt

$\Delta G^0 = -nFE^0_{cell}$ $\{-2\times 96500\times 1.23\}$ J

$\because$ Work derived from this fuel cell = $\frac{70}{100}\times(-\Delta G^0_{cell})\times 1.0\times 10^{-3} = x$ J

Since insulated vessel, hence q = 0

From equation, for monoatomic gas,

$w = \Delta U \Rightarrow x = nC_{V,m}\Delta T$; $\left\{C_{V,m} = \frac{3R}{2}\right\}$

Or $\frac{70}{100}\times 2\times 96500\times 1.23\times 10^{-3} = 1\times\frac{3}{2}\times 8.314\times\Delta T$

$\Delta T = 13.32$

16. Aluminium reacts with sulfuric acid to form aluminium sulfate and hydrogen. What is the volume of hydrogen gas in liters (L) produced at 300 K and 1.0 atm pressure, when 5.4 g of aluminium and 50.0 mL of 5.0 M sulfuric acid are combined for the reaction? (Use molar mass of aluminium as 27.0 g mol^{-1}, R = 0.082 atm L mol^{-1} K^{-1})

Answer: 6.15 Litre

Solution:

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$

Mole of Al taken = $\frac{5.4}{27} = 0.2$

Mole of H_2SO_4 taken = $\frac{50 \times 5}{1000} = 0.25$

As $\frac{0.2}{2} > \frac{0.25}{3}$, H_2SO_4 is limiting reagent

Now, moles of H_2 formed = $\frac{3}{3} \times 0.25 = 0.25$

$\therefore$ Volume = $\frac{0.25 \times 0.082 \times 300}{1} = \frac{24.6}{4} = 6.15$ L

17. ${}^{238}_{92}U$ is known to undergo radioactive decay to form ${}^{206}_{82}Pb$ by emitting alpha and beta particles. A rock initially contained 68 × 10^{-6} g of ${}^{238}_{92}U$. If the number of alpha particles that it would emit during its radioactive decay of ${}^{238}_{92}U$ to ${}^{206}_{82}Pb$ in three half-lives is $Z \times 10^{18}$, then what is the value of Z?

Answer: 1.21

Solution:

$${}_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8\,{}_{2}He^{4} + 6\,{}_{-1}\beta^{0}\,(\text{antineutrino})$$

Initial mole of U^{238} = $\left[\frac{68 \times 10^{-6}}{238}\right] = x$

Mole of U^{238} decayed in three half-lives = $\frac{7}{8}x$

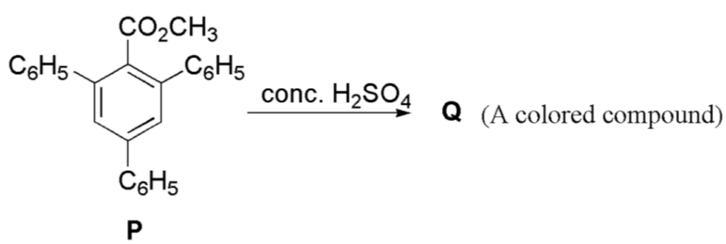
In decay from U^{238} to Pb^{206}, each U^{238} atom decays and produces 8α-particles and hence, total number of α-particles emitted out = $\left(\frac{7}{8}x\right) \times 8 \times N_A$

$= \frac{7}{8} \times \frac{68 \times 10^{-6}}{238} \times 8 \times 6.022 \times 10^{23}$

$= 1.2046 \times 10^{18}$

= 1.21

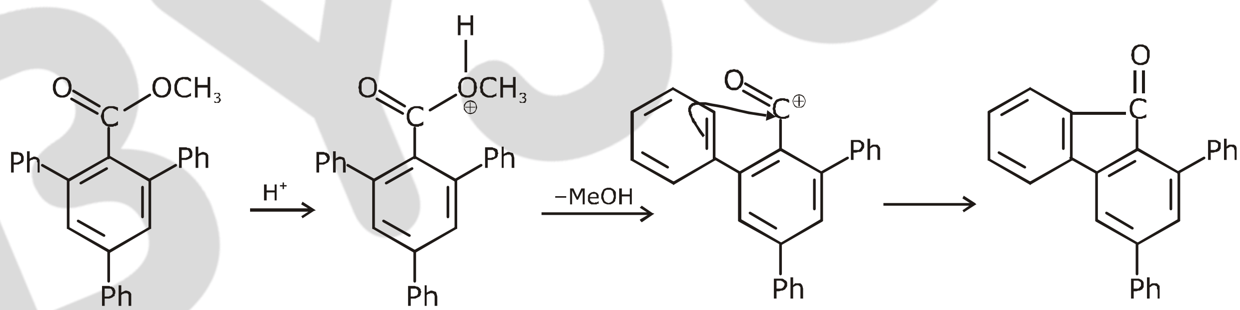
18. In the following reaction, compound **Q** is obtained from compound **P** via an ionic intermediate.



What is the degree of unsaturation of **Q**?

Answer: 18

Solution:



Total degree of unsaturation = 18