

# Department of Examinations - Sri Lanka <br> G.C.E. (A/L) Examination - 2018 

## 02 - Chemistry

## Marking Scheme



This document has been prepared for the use of Marking Examiners. Some changes would be made according to the views presented at the Chief Examiners' meeting.
40. Which of the following statements is/are correct with regard to the nitrogen cycle?
(a) $\mathrm{N}_{2}$ in the atmosphere is fixed only by atmospheric and industrial fixation.
(b) $\mathrm{N}_{2}$ is reduced during atmospheric fixation.
(c) $\mathbf{N}_{2}$ is oxidized during industrial fixation.
(d) Nitrates and nitrites formed during atmospheric fixation are utilized by plants to make proteins when the rainfall deposil them on the ground.

- In question Nos. 41 to 50 , two statements are given in respect of each question.

From the Table given below, select the response out of the responses (1), (2), (3), (4) and (5) that best firs the two statements and mark appropriately on your answer sheet.

| Response | First Statement | Second Statement |
| :---: | :--- | :--- |
| $(1)$ | True | True, and correctly explains the first statement |
| $(2)$ | True | True, but does not explain the first statement correctly |
| $(3)$ | True | False |
| $(4)$ | False | True |
| $(5)$ | False | False |


| 41. | First Statement |
| :--- | :--- |
| BaCO | is more thermally slable than $\mathrm{MgCO}_{3}$. | | Polarizing power of group two cations decreases |
| :--- |
| down the group. |

amine has a lower tendency so form a bond
with $\mathrm{H}^{+}$, than the lone pair of electrons on oxygen in an alcohol.
43. A reaction at equilibrium can be driven fonward (ie. shift of equilibrium point to the right) by adding a catalyst.
44. $\mathrm{CO}_{3}^{2-}$ and $\mathrm{SO}_{3}^{2-}$ ions have similar shapes.
45. The boiling point of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ is higher than the boiling points of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ and $\mathrm{CH}_{3} \mathrm{COCH}_{3}$
46. A reaction occurring spontaneously in an isolated system always has a negative Gibbs energy change.
47. Commonly used soap contain the sodium or potassium salts of fatty acids formed by the reaction of NaOH or KOH with oils and fats.
48. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Br}$ does not react easily with NaOH to form $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}$.
49. When an aqueous solution of a weak acid is diluted. both the fraction of dissociated acid molecules and pH of the medium are increased.

Dissociation of weak acid molecules occur itu such a way that the acid dissociation constant $K_{\mathrm{a}}$ remairs constant.
Increase of $\mathrm{CO}_{2}$ Ievel in the atmosphere cannot be controlled by green plants.

இல்ங்கைப் பரீட்ணைத் திணைாக்களாம்



I ठஇா／ుத்திரம் I

| Batb <br>  வิ｜ळा இல． | 88ox Come ヘி゙あっ 8ல． | B（5ేe） 표N விळा 800. | 88cyor Fomb விตை囚ఱ． | 回ばロ 80\％M வி｜6ฺा 80. | 88qú 40\％0 விळை （30）． | Bose BㅇN） விตणा இல． | B8qd floturs ธilcol இ00． | 900 ERDM விळึा 8ல． | 880 ctotive ヘி｜cㄴ 800． |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 01. | ． 04. | 11. | －－－3．－ | 21. | ．．．2．．． | 31. | $\ldots$ | 41. | 1 |
| 02. | $\underset{\text { both }}{1 \text { or } 5 \mathrm{gr}}$ | 12. | 4 | 22. | 4 | 32. | 5 | 42. | 4 |
| 03. | 2 | 13. | 1 | 23. | 5 | 33. | 3 | 43. | 5 |
| 04. | 5 | 14. | 3 | 24. | 4 | 34. | －－． 5 | 44. | ． 5 |
| 05. | 2 | 15. | 3 | 25. | 1 | 35. | ＿． 4 | 45. | ． 2 |
| 06. | 1 | 16. | $3$ | 26. | 3 | 36. | 1 or 5 or both | 46. | ．．． 4. |
| 07. | 4 | 17. | 2 | 27. | 1 | 37. | 5 | 47. | 1 |
| 08. | 2 | 18. | 4 | 28. | 4 | 38. | 2 | 48. | 3 |
| 09. | 5 | 19. | 2 | 29. | 3 | 39. | 3 | 49. | ．．． 1 |
| 10. | －． 2 | 20. | 2 | 30. | ．．．1．．．． | 40. | 5 | 50. | 3 |





PART A - STRUCTURED ESSAY
Answer all four questions on this paper ilself. (Each question carries 10 marks)

1. (a) State whether the following statements are true or false, (Reasons are not required.)
(i) The polarizability of halide ions increases with increasing size.

True.......
(ii) The $\mathrm{O}-\mathrm{N}-\mathrm{O}$ bond angle of $\mathrm{NO}_{2}$ is greater than that of $\mathrm{NO}_{2}^{-}$.
(iii) London dispersion forces among $\mathrm{CCl}_{4}$ molecules are smaller than the London dispersion forces among $\mathrm{SO}_{3}$ molecules.
(iv) The shape of the $\mathrm{HSO}_{4}^{-}$iun is trigonal bipyramidal.
(v) All $3 d$ atomic orbitals of an atom are represented by quantum numbers $\left(n, l, m_{l}\right) 3,2,1$.
(vi) The addition of an elecuron to a gaseous phosphorus atom is an exothermic process whereas for a gascous nitrogen atom it is endothermic.

## True

False

False
False

True True.
( $\checkmark=$ True $\quad X=$ False can be accepted.)
(04 marks $\times 6=24$ )

$$
1(a)=24 \text { marks }
$$

(b) (i) Draw the most acceptable Lewis structure for the molecule $\mathrm{SF}_{3} \mathrm{~N}$.

(ii) The most stable Lewis structure for the molecule $\mathrm{C}_{3} \mathrm{O}_{2}$ (carbon suboxide) is shown below. Draw another two Lewis structures (resonance structures) for this molecule.
(Note: Marks will not be awarded for Lewis srructures drawn with octel nule violated)

$$
\ddot{\mathrm{O}}=\mathrm{C}=\mathrm{C}=\mathrm{C}=\stackrel{\mathrm{O}}{\mathrm{C}}
$$


(any two)
(07 marks x $2=14$ )
(resonance arrows are not required for award of marks)
(iv) In each of the following instances, give a balanced chemical equation to indicate the action of $\mathbf{Y}$.
I. Y as an oxidizing agent

$$
\begin{aligned}
& 2 \mathrm{Na}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{l}) \rightarrow 2 \mathrm{NaNH}_{2}(\mathrm{~s})+\mathrm{H}_{2}(\mathrm{~g}) \\
& 3 \mathrm{Mg}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{l}) \rightarrow \mathrm{Mg}_{3} \mathrm{~N}_{2}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) \\
& 6 \mathrm{Li}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{l}) \rightarrow 2 \mathrm{Li}_{3} \mathrm{~N}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) \\
& (\text { Any one })
\end{aligned}
$$

II. Y as a reducing agent

$$
\begin{aligned}
& 3 \mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+6 \mathrm{HCl}(\mathrm{~g}) \\
& 3 \mathrm{Cl}_{2}(\mathrm{~g})+8 \mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+6 \mathrm{NH}_{4} \mathrm{Cl}(\mathrm{~s}) \\
& 3 \mathrm{Cl}_{2}(\mathrm{~g})+\mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \mathrm{NCl}_{3}(\mathrm{l})+3 \mathrm{HCl}_{(\mathrm{g})}(\mathrm{g}) \\
& 3 \mathrm{CuO}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{Cu}(\mathrm{~s})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
& 3 \mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow 2 \mathrm{~N}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& 5 \mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow 4 \mathrm{NO}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& \text { (Any one) }
\end{aligned}
$$

Note: Physical states are not required for award of marks.
(v) Consider the hydrides of the elements in the group to which $\mathbf{X}$ belongs, which are analogous to $\mathbf{Y}$. Sketch the variation in boiling points of these hydrides (including $\mathbf{Y}$ ) in the graph below. In your sketch indicate the hydrides using their chemical formulae. (Note: Values of boiling points are not required.)


Note: Shape (02). Shape needs to be correct for award of marks for labeling.
(i.e. Max. $\mathrm{SbH}_{3}$; Min. $\mathrm{PH}_{3}$; In between $\mathrm{NH}_{3}$ )
(vi) Give reasons for the variation in boiling points in part (v) above. As molecular mass / size increases, boiling point increases.
But with $\mathrm{NH}_{3}$, boiling point is higher than expected because
of H -bonding between $\mathrm{NH}_{3}$ molecules.
(yii) I. Write what you would observe when an excess of an aqueous solution of $\mathbf{Y}$ is added to a solution of $\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$.
.white precipitate. / white gelatinous precipitate
I. Write the chemical formula of the species that gives rise to your observation in part I above.
........ Al( OH$)_{3}$ (03)
(viii) Give one chemical test to identify $\mathbf{Y}$.

Test: $\quad$ Test with Nessler's reagent
Brown precipitate / Brown coloration
Observation :
OR
Test with HCl vapour
White fumes

OR

Test with red litmus
Red litmus turns blue

OR
Add to a solution of $\mathrm{Cu}(\mathrm{II})$ ions
Deep blue colour solution
(ix) $\mathbf{Z}$ is an oxo-acid of $\mathbf{X}$ and a strong oxidizing agent.
I. Identify $\mathbf{Z}$.
$\mathrm{HNO}_{3}$ OR Nitric acid
II. State the products obtained when hot concentrated $\mathbf{Z}$ reacts with sulphur. $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{l}), \mathrm{NO}_{2}(\mathrm{~g}), \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

Note: physical states are not required.

$$
2(a)=60 \text { marks }
$$

(b) A and $\mathbf{B}$ are compounds of two $p$-block elements that belong to the same group in the Periodic Table. A exists as a colourless, odourless liquid at room temperature and atmospheric pressure. It is also found in the gaseous and solid states. The solid state of $\mathbf{A}$ is less dense than its liquid state. Ionic and polar compounds are readily soluble in $\mathbf{A}$.
B is a colourless gas at room temperature and atmospheric pressure. A filter paper moistened with lead acetate turas black on treatment with B.
(i) Identify $\mathbf{A}$ and B .
A. $\mathrm{H}_{2} \mathrm{O} \quad$ B- $\mathrm{H}_{2} \mathrm{~S}$
$(04+04)$
(ii) Sketch the shapes of $\mathbf{A}$ and $\mathbf{B}$ showing lone pairs of electrons where necessary.


A


B
$(03+03)$
(iii) Giving reasons, state whether $\mathbf{A}$ or $\mathbf{B}$ has the larger bond angle.

Oxygen is more electronegative than suphur.
Therefore, bonding pairs of electrons are located closer to
the oxygen atom in $\mathrm{H}_{2} \mathrm{O}$, than to the sulphur atom in $\mathrm{H}_{2} \mathrm{~S}$.
Therefore, repulsion of bonding electron pairs is greater
in $\mathrm{H}_{2} \mathrm{O}$ than in $\mathrm{H}_{2} \mathrm{~S}$.
Bond angle of $\underset{A}{ } / \mathrm{H}_{2} \mathrm{Ois}$ greater than bond angle of $\mathrm{B} / \mathrm{H}_{2} \mathrm{~S}$
(iv) In each of the following instances, give a balanced chemical equation to indicate the action of $\mathbf{A}$.
I. $A$ as an acid

$2 \mathrm{Na}(\mathrm{s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow 2 \mathrm{NaOH}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})$
(OR any other metal that reacts with water liberating $\mathrm{H}_{2}$ )
(Note: $\longrightarrow$ accepted)
II. A as a base:

$$
\begin{align*}
& \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{HCl}(\mathrm{aq}) \quad \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \quad \text { OR }  \tag{03}\\
& \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})
\end{align*}
$$

(v) Write the balanced chemical equation for the reaction of $\mathbf{B}$ with aqueous lead acetate.

$$
\begin{equation*}
\mathrm{Pb}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) \longrightarrow \mathrm{PbS}(\mathrm{~s})+2 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \tag{03}
\end{equation*}
$$

$\left(\mathrm{OR}^{-2 \mathrm{CH}} \mathrm{H}_{3} \mathrm{COO} \cdot+{ }^{-2 H}+\right.$
(vi) I. Write what you would observe when $\mathbf{A}$ and $\mathbf{B}$ are added separately to an acidified solution of $\mathrm{BiCl}_{3}$.
with $\boldsymbol{A}$ (excess) - white precipitate / white solid/ white turbidity
with B $\quad$ - black precipitate
II. Write balanced chemical equations for your observations in part I above.
$\mathrm{BiCl}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longrightarrow \mathrm{BiOCl}(\mathrm{s})+2 \mathrm{HCl}(\mathrm{aq})$
$(\rightarrow \cdots$ can be accepted.)

Note: Physical states are not required for parts (iv), (v), (vi)
3. The reaction $\mathbf{A}+\mathrm{B}=2 \mathrm{C}+\mathbf{D}$ (elementary in both directions) was carried out at $25^{\circ} \mathrm{C}$. Initially, the reaction mixture was made by dissolving 0.10 mol of $\mathbf{A}$ and 0.10 mol of $\mathbf{B}$ in distilled water (total ; volume $100.00 \mathrm{~cm}^{3}$ ). Variation in the concentration of $\mathbf{A}$ in this solution with time is shown in the graph.

(i) Calculate the amount of A (in moles) reacted during the first 4.0 minutes of the reaction.

Initial amount of A
Concentration of A after 4.0 min
Amount of $A$ reacted

$$
\begin{aligned}
& =0.1 \mathrm{~mol} \\
& =0.75 \mathrm{~mol} \mathrm{dm}^{-3} \\
& =(0.1-0.75) \times 100 \times 10^{-3} \mathrm{~mol} \\
& =0.025 \mathrm{~mol}
\end{aligned}
$$

(ii) Would the rate of the forward reaction be less than the rate of the reverse reaction after 4.0 minutes? Explain your answer.
No.

Forward and reverse rates will be equal after 4.0 min .
OR The reaction has reached the equilibrium.
(iii) Given that the rate constant of the forward reaction ( $k_{\text {forwart }}$ ) is $18.57 \mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~min}^{-1}$, calculate the initial rate of the forward reaction.

Rate of the forward reaction, $\mathrm{B}_{\mathrm{F}}=\mathrm{k}[\mathrm{A} \mid[\mathrm{B}]$
 (04+01) $=18.57 \mathrm{~mol} \mathrm{dm} \mathrm{m}^{-3} . \mathrm{min}^{-1}$
(iv) Calculate the concentrations of C and D at equilibrium.

Draw the relevant curves showing the variation of the concentrations of $\mathbf{C}$ and $\mathbf{D}$ with tirts in the above graph and label them.

| Contentration of. C, at equilibrium. | . $025 . \mathrm{mol} / 100.00 \times 10^{-3}$ | 1) |
| :---: | :---: | :---: |
|  | $=0.50 \mathrm{~mol} \mathrm{dm}^{-3}$ | (02+01) |
|  |  | ( $02+0{ }^{\text {a }}$ 1) |
|  | = $0.25 \cdot \mathrm{moldm} \mathrm{m}^{3}$ | (02+01) |



Curve C
Curve D
(04)
(04)

Note : Do not award marks if the curves do not become flat after 4.0 min , if the curves do not reach the respective concentrations at 4.0 min , If the curves for $C$ and $D$ are not labeled and if the curves do not start from zero.
(v) Write the expression for the equilibrium constant $K_{c}$ of the above reaction and calculate its
value.
$\quad$ (Equilibrium constant), $K_{c}=\frac{[C]^{2}[D]}{[A]][B]}$
$. K_{\varepsilon}=\frac{\left(0.5 \mathrm{~mol} d m^{-3}\right)^{2}\left(0.25 \mathrm{~mol} d m^{-3}\right)}{\left(0.75 \mathrm{miot}\left(d \mathrm{~m}^{2-9}\right)\left(0.75 \mathrm{miol} d \mathrm{~m}^{2 / 3}\right)\right.}$

$$
k_{c}=1.11 \times 10^{-1} \text { mol dm }
$$

(vi) Calculate the value of the rate constant ( $k_{\text {reversis }}$ ) of the reverse reaction.

$$
k_{T}=1.67 \times 10^{2} \mathrm{~mol}^{-2} \mathrm{dm}{ }^{6} \mathrm{~min}^{-1}
$$

(vii) After reaching equilibrium, the volume of the solution was doubled by adding $100.00 \mathrm{~cm}^{3}$ of distilled water. Prediet the direction of the net reaction soon after doubling the volume of the solution, by means of a suitable calculation.

## New concentrations,

$[A]=0.75 / 2 \mathrm{~mol} \mathrm{dm}^{-3},[\mathrm{~B}]=0.75 / 2 \mathrm{~mol} \mathrm{dm}^{-3},[\mathrm{C}]=0.5 / 2 \mathrm{~mol} \mathrm{dm}^{-3},[\mathrm{D}]=0.25 / 2 \mathrm{~mol} \mathrm{dm}^{-3}$
Rate of forward reaction,

$$
\begin{aligned}
\mathrm{R}_{i} & =18.57 \mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~min}^{-1}\left(0.75 / 2 \mathrm{~mol} \mathrm{dm}^{-3}\right)^{2} \\
& =2.61 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~min}^{-1}
\end{aligned}
$$

Rate of the reverse reaction,

$$
\begin{aligned}
\mathrm{R}_{\mathrm{r}} & =1.67 \times 10^{2} \mathrm{~mol}^{-2} \mathrm{dm}^{6} \mathrm{~min}^{-1}\left(0.5 / 2 \mathrm{~mol} \mathrm{dm}^{-3}\right)^{2}\left(0.25 / 2 \mathrm{~mol} \mathrm{dm}^{-3}\right) \\
& =1.30 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~min}^{-1}
\end{aligned}
$$

$\mathrm{R}_{\mathrm{P}}>\mathrm{R}_{\mathrm{r}}$ Net reaction occurs in the forward direction,

## Alternate answer

$\left.\left.Q=\frac{\left(\frac{05}{2} \text { mol dm }\right.}{}{ }^{-3}\right)^{2}\left(\frac{0.25}{2} \mathrm{~mol} \mathrm{dm}^{-3}\right)\right)$
$Q=0.056 \mathrm{~mol} \mathrm{dm}{ }^{-3}$
$Q<K$, therefore, the net reaction occurs in the forward direction.
(viii) Consider that the above experiment was conducted at a temperalure lower than $25^{\circ} \mathrm{C}$. How would this affect the rate of the reverse reaction? Explain your answer giving reasons. Rate of the reverse reaction will decrease

## Because

 decreases.
and
the collision rate decreases.

$$
\text { Q3 = } 100 \text { marks }
$$

4. (a) (i) Compounds A, B and C are structural isomers of each other having the molecular formula $\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{O}$. All three compounds give ycllow-orange precipitates with 2,4 -DNP. None of them give a silver mirror in the silver mirror test. When $\mathbf{A}, \mathbf{B}$ and $\mathbf{C}$ were separately reacted with $\mathrm{NaBH}_{4}$, compounds D, E and $\mathbf{F}$ respectively were obtained. Only $\mathbf{E}$ and $\mathbf{F}$ showed optical isomerism. When $\mathbf{B}$ and $\mathbf{C}$ were separately reacted with $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{MgBr}$ followed by hydrolysis, compounds $\mathbf{G}$ and H respectively, were obrained. Only G showed optical isomerism. Draw the structures of A. B, C, D, E, F, G and H in the boxes given below. ( It is not necessary to show stereoisomeric forms.)


A


D


G


B


E


H


C


Note: $\mathrm{C}_{3} \mathrm{H}_{7}$ can be accepted in place of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2}$. $\mathrm{C}_{2} \mathrm{H}_{5}$ can be accepted in place of $\mathrm{CH}_{3} \mathrm{CH}_{2}$.
(05 marks x $8=40$ marks)

Note: A, B. C should be correct to award marks for D. E. F B, C should be correct to award marks for $\mathrm{G}, \mathrm{H}$
(ii) Draw the structure of the product of the following reaction.

$\xrightarrow[\text { (2) dehydration }]{\text { (1) } 2,4-\text { DNP }}$


Note : Lone pairs are not necessary. Award mark if B or C is used instead of A,with the correct corresponding product.
(b) Draw the structure of the major organic product in each of the following reactions.

| (i) $\mathrm{C}_{6} \mathrm{H}_{6}$ | $\xrightarrow[150^{\circ} \mathrm{C}]{\mathrm{H}_{2} / \text { Raney Ni }}$ | $0$ | (04) |
| :---: | :---: | :---: | :---: |
| (ii) $\mathrm{C}_{6} \mathrm{H}_{5}-\mathrm{NH}_{2}$ | $\xrightarrow{\mathrm{Br}_{2} \text { water }}$ |  | (04) |
| (iii) $\mathrm{CH}_{3} \mathrm{CHO}$ | (1) aqueous NaOH <br> (2) dehydration |  | (04) |
|  |  |  | 1 |
| (iv) $\mathrm{C}_{6} \mathrm{H}_{5}-\mathrm{N}_{2} \mathrm{Cl}^{\text {Cl }}$ | $\xrightarrow[\Delta]{\mathrm{H}_{3} \mathrm{PO}_{2}}$ | $\circlearrowleft$ | (04) |
| (v) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CONH}_{2}$ | $\xrightarrow[\Delta]{\text { aqueous } \mathrm{NaOH}}$ |  | (04) |
| (vi) $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH}_{2}$ | conc. $\mathrm{H}_{2} \mathrm{SO}_{4} \longrightarrow$ |  | (03) |
| (vii) $\mathrm{CH}_{3} \mathrm{COCl}$ | $\xrightarrow{\mathrm{NH}_{3}}$ |  | (03) |
| (viii) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}$ | $\mathrm{PCl}_{5}$ |  | (03) |
| (ix) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ | $\mathrm{H}^{+} / \mathrm{KMnO}_{4} \longrightarrow$ | $\mathrm{CH}_{3} \mathrm{COOOH}$ | (03) |
| (x) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COCH}_{3}$ | $\xrightarrow{\mathrm{HCN}}$ |  | (03) |

(i) strcture showing hydrogens on $\bigcirc$ can be accepted.
(iii) $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCHO}$ can be accepted. No marks for $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOH}$
(iv) can be acepted
(v) Charges on O and Na are not required for award of marks. No marks if given as O — Na
(vi) $\mathrm{OSO}_{2} \mathrm{OH}$ can be accepted.
(vii) $\mathrm{CH}_{3} \mathrm{CONH}_{2}$ can be accepted.
(viii) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COCl}$ can be accepted.
(ix) $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ can be accepted.


4.(c): 20 marks

Note: if no half arrow are drawn, deduct (01) mark once in each line.
Radical needs to be shown for award of marks.
Mark each step as an independent step.

## PART B - ESSAY

Answer fwo questions only. (Each question carries 15 marks.)
5. (a) Consider the following reactions.

$$
\begin{aligned}
& \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \mathrm{nH}_{2} \mathrm{O}(\mathrm{~s}) \rightarrow \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{~s})+\mathrm{aH}_{2} \mathrm{O}(\mathrm{~g}) \\
& \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{MO}_{2}(\mathrm{~s})+2 \mathrm{CO}_{2}(\mathrm{~g})
\end{aligned}
$$

A small amount ( 0.10 mol ) of $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \cdot \mathrm{nH}_{2} \mathrm{O}$ (s) is present in an evacuated rigid container of volume $0.08314 \mathrm{~m}^{3}$. The temperature of the container was raised to 400 K . The metal carbonate, $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}$ does not decompose at this temperature but the crystalline water evaporates completely. The pressure of the container was measured to be $1.60 \times 10^{4} \mathrm{~Pa}$. Volume occupied by the solids is negligible.
Determine the value of " $n$ " in the formula $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \cdot{ }^{n} \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$.

$$
\begin{aligned}
& \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \cdot \mathrm{nH}_{2} \mathrm{O}(\mathrm{~s}) \rightarrow \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{~s})+\mathrm{nH} \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
& \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{MO}_{2}(\mathrm{~s})+2 \mathrm{CO}_{2}(\mathrm{~g})
\end{aligned}
$$

The amount of $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \cdot \mathrm{nH}_{2} \mathrm{O}$ used $=0.10 \mathrm{~mol}$
Water is completely evaporated.
Using $P V=n R T$,
$n_{H 2 O}=\frac{1.60 \times 10^{4} \mathrm{~Pa} \times 0.08314 \mathrm{~m}^{3}}{8.314 \mathrm{~J} \mathrm{~mol}}{ }^{-1} \mathrm{~K}^{-1} \times 400 \mathrm{~K}$ $=0.40 \mathrm{~mol}$
0.1 mol of $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}, \mathrm{nH}_{2} \mathrm{O}$ (s) has generated 0.40 mol of $\mathrm{H}_{2} \mathrm{O}$. Therefore, $\mathrm{n}=4$

$$
5(\mathrm{a})=20 \text { marks }
$$

(b) The temperature of the above system was then increased to 800 K . It was observed that some amount of the solid metal carbonate is decomposed and is in equilibrium with the gas phase. The pressure of the container was measured to be $4.20 \times 10^{4} \mathrm{~Pa}$,
(i) Calculate the partial pressure of water vapour in the container at 800 K .

Partial pressure of $\mathrm{H}_{2} \mathrm{O}$ at 800 K ,

$$
\begin{aligned}
& P_{H 2 O}=\frac{\pi_{H 2 O} R T}{V} \\
& =\frac{0.4 \mathrm{~mol} \times 8.314 \mathrm{Jmol} l^{-1} \mathrm{~K}^{-1} \times 800 \mathrm{~K}}{0.08314 \mathrm{~m}^{3}} \\
& =3.20 \times 10^{4} \mathrm{~Pa}
\end{aligned}
$$

## Alternate Answer 01

$$
\begin{align*}
& \text { Total pressure at } 800 \mathrm{~K}, \mathrm{P}_{\mathrm{T}}=4.20 \times 10^{4} \mathrm{~Pa} \\
& \text { Total number of moles } \mathrm{n}_{\mathrm{T}}= \frac{4.20 \times 10^{4} \mathrm{~Pa} \times 0.08314 \mathrm{~m}^{3}}{8.314 \mathrm{~J} \mathrm{~mol}}  \tag{04+01}\\
&=0.525 \mathrm{~mol} \\
& \text { Partial pressure of water } \begin{aligned}
-1
\end{aligned} \mathrm{B00K} \\
&=\mathrm{P}: \mathrm{q} 20 \\
&=3.20 \times 1 \mathrm{P}_{\mathrm{T}} \times \mathrm{H} 20
\end{align*}
$$

## Alternate Answer 02

Because V and $\mathrm{m}_{\mathrm{H} 20}$ are constant, at 800 K ,
partial pressure of water $=\mathrm{P}_{\mathrm{HzO}}=2 \times 1.60 \times 10^{4} \mathrm{~Pa}$

$$
=3.20 \times 10^{4} \mathrm{~Pa}
$$

(ii) Calculate the partial pressure of $\mathrm{CO}_{2}$ in the container at 800 K .

Partial pressure of $\mathrm{CO}_{2}$ at 800 K ,

$$
\begin{aligned}
P_{C O 2} & =P_{\text {total }}-P_{\mathrm{H} 2 O} \\
& =4.2 \times 10^{4} \mathrm{~Pa}-3.2 \times 10^{4} \mathrm{~Pa} \\
& =1.00 \times 10^{4} \mathrm{~Pa}
\end{aligned}
$$

(iii) Write an expression for the pressure equilibrium constant, $K_{\mathrm{p}}$ for the decomposition of
$\mathrm{M}(\mathrm{CO})$ (s). Calculate $K$ at 800 K . $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}$ (s). Calculate $K_{\mathrm{p}}$ at 800 K .

$$
\begin{align*}
& K_{P}=P^{2} C O 2  \tag{05}\\
& K_{P}=\left(1.0 \times 10^{4} \mathrm{~Pa}\right)^{2}=1.00 \times 10^{8} \mathrm{~Pa}^{2} \tag{04+01}
\end{align*}
$$

(iv) Calculate the molar percentage of the metal carbonate decomposed at $800^{\prime} \mathrm{K}$,

Initial amount $=0.10 \mathrm{~mol}$
Amount of $\mathrm{CO}_{2}$ generated $=\mathrm{ncoz}^{2}$
$n_{\mathrm{CO2}}=\frac{P_{\mathrm{CO} 2} V}{R T}$
$n_{C O 2}=\frac{1.0 \times 10^{4} \mathrm{~Pa} \times 0.08314 \mathrm{~m}^{3}}{8.314 / \mathrm{mol}^{-1} \mathrm{~K}^{-1} \times 800 \mathrm{~K}}$ or $\frac{3.2 \times 10^{4} \mathrm{~Pa}}{1.0 \times 10^{4} \mathrm{~Pa}}=\frac{0.4}{n_{\mathrm{CO} 2}}$
$n_{\mathrm{CO2}}=0.125 \mathrm{~mol}$
Amount of $\mathrm{M}\left(\mathrm{CO}_{3}\right)_{2}$ decomposed $=1 / 2$ amount of $\mathrm{CO}_{2}$ generated .

$$
\begin{equation*}
\mathrm{mol} \% \text { of } \mathrm{M}\left(\mathrm{CO}_{3}\right)_{2} \text { decomposed }=\frac{0.0625 \mathrm{~mol}}{0.10 \mathrm{~mol}} \times 100 \tag{03}
\end{equation*}
$$

$$
\begin{equation*}
=62.5 \% \tag{02}
\end{equation*}
$$

(v) Enthalpy change $(\Delta H)$ for the decomposition of the metal carbonate under the above conditions is $40.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Calculate the comesponding entropy change ( $\Delta \mathrm{S}$ ).
Sysiem is at equilibrium, therefore $\Delta \mathrm{G}=0$.
$\Delta S=\frac{\Delta H}{T}$
$\Delta S=\frac{40.0 \times 10^{3} \mathrm{~J} \mathrm{~mol}}{} \mathrm{~mol}^{-1}$
$\Delta S=50.0 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ OR $0.05 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
Note : $\Delta S^{0}, \Delta H^{0}$ cannot be accepted.
(vi) Suggest two ways to drive the decomposition reaction of $M\left(\mathrm{CO}_{3}\right)_{2}$ (s) in the forward direction.

Increase temperature
Remove $\mathrm{CO}_{2}$

$$
5 \text { (b) = } 65 \text { marks }
$$

(c) With the aid of thermochemical cycles and the data given in the table, answer the following questions.

| Species | Standard enthalpy of formation $\left(\Delta H_{f}^{\circ}\right)\left(\mathrm{kJ} \mathrm{mol}^{-\mathrm{b}}\right)$ |
| :---: | :---: |
| $\mathrm{M}(\mathrm{s})$ | 0.0 |
| $\mathrm{M}(\mathrm{g})$ | 800.0 |
| $\mathrm{O}_{2}(\mathrm{~g})$ | 0.0 |
| $\mathrm{O}(\mathrm{g})$ | 249.2 |
| $\mathrm{MO}_{2}(\mathrm{~g})$ | -400.0 |

(i) Given that $\mathrm{MO}(\mathrm{g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{MO}_{2}(\mathrm{~g}) \Delta \mathrm{H}^{\circ}=-50.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$, calculate the standard enthalpy of formation of $\mathrm{MO}(\mathrm{g})$.

$(02+02+02=06)$
Note : To award marks for the cycle, reactions must be balanced and physical states must be given. r

$$
\begin{aligned}
& \text { Standard formation enthalpy of } \mathrm{MO}(\mathrm{~g}), \Delta H_{\mathrm{f}}^{0} \\
& \begin{aligned}
\Delta \mathrm{H}_{\mathrm{I}}^{0} & =(-400.0+50.0) \mathrm{kJ} \mathrm{~mol} \\
& =-350.0 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
\end{aligned}
$$

(ii) Calculate $\mathrm{M}-\mathrm{O}$ bond dissociation enthalpy in $\mathrm{MO}(\mathrm{g})$.


$$
(02+02+02+02=08)
$$

Note : To award marks for the cycle, reactions must be balanced and physical states must be given.
MO bond dissociation enthalpy change $=\Delta H_{x}{ }^{0}$

$$
\begin{aligned}
\Delta H_{x}^{0} & =(350.0+800.0+249.2) \mathrm{kJ} \mathrm{~mol} \\
& =1399.2 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

(iii) Calculate $\mathrm{M}-\mathrm{O}$ bond dissociation enthalpy in $\mathrm{MO}_{2}(\mathrm{~g})$.

(02+02+02+02 =08)
Note : To award marks for the cycle, reactions must be balanced and physical states must be given.

$$
\begin{aligned}
& \Delta H_{Y}^{0}=(400.0+800.0+2 \times 249.2) \mathrm{kJ} \mathrm{~mol}^{-1} \\
&=1698.4 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \text { MO bond dissociation energy in } \mathrm{MO}_{2}=1 / 2 \Delta \mathrm{H}_{v}^{0}=849.2 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

[04+01)
(04+01)
(iv) By means of a suitable calculation, predicl whether the reaction, $\mathrm{MO}_{2}(\mathrm{~g}) \rightarrow \mathrm{MO}(\mathrm{g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ is spontaneous under standard conditions and 2000 K . Standard entropy change of this reaction is $30.0 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$,

$$
\begin{aligned}
& \Delta G^{0}=\Delta H^{0}-T \Delta S^{0} \\
& \text { For the reaction, } \mathrm{MO}_{2}(\mathrm{~g}) \longrightarrow \mathrm{MO}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \quad \text { at } 2000 \mathrm{~K} \text {, } \\
& \Delta G^{0}=50.0 \times 10^{3} \mathrm{~J} \mathrm{~mol}^{-1}-2000 \mathrm{~K} \times 30.0 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
& =-10000.0 \mathrm{~J} \mathrm{~mol}^{-1}=-10.0 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

The given reaction is spontaneous at 2000 K .

## Note : Standard states are required for award of marks.

$$
5(\mathrm{c})=65 \text { marks }
$$

6. (a) An experiment was carried out to determine the partition coefficient of jodine ( $l_{2}$ ) berween waser (A) and an organic solvent (B) which form an immiscible liquid system.
$20.00 \mathrm{~cm}^{3}$ of $\mathbf{B}$ containing ' $n$ ' moles of $\mathrm{I}_{2}$ is mixed with $20.00 \mathrm{~cm}^{3}$ of $A$ and allowed to reach equilibrium at room temperature.
The concentration of $\mathrm{I}_{2}$ in phase A is determined by titrating a $5.00 \mathrm{~cm}^{3}$ sample drawn from phase $A$ with a 0,005 moldm ${ }^{-3}$ solution of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$. The volume of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ required to reach the end point was $22.00 \mathrm{~cm}^{3}$. The concentration of $\mathrm{I}_{2}$ in phase $\mathbf{B}$ was determined to be $0.040 \mathrm{~mol} \mathrm{dm}^{-3}$.
(i) Write the balanced chemical equation for the reaction between $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ and $\mathrm{I}_{2}$.

(ii) Calculate the concentration of $\mathrm{I}_{2}$ in phase A .

$$
\text { Concentration of } \begin{aligned}
\mathrm{I}_{2} \text { in phase } \begin{aligned}
& A=\frac{22.00 \mathrm{~cm}^{3} \times 0.005 \mathrm{~mol} \mathrm{dm}}{}{ }^{-3} \\
& 2 \times 5.0 \mathrm{~cm}^{3} \\
&=0.011 \mathrm{~mol} \mathrm{dm}^{-3}
\end{aligned},
\end{aligned}
$$

(iii) Calculate the value of the partition coefficicnt, $K_{D}$ where $K_{D}=\frac{\left[1_{2}\right]_{B}}{\left[1_{2}\right]_{A}}$,

Partition coefficient, $K_{D}=\frac{\left[I_{2}\right]_{B}}{\left[I_{2}\right]_{A}}=\frac{0.04 \mathrm{~mol} \mathrm{dm}^{-3}}{0.011 \mathrm{~mol} \mathrm{dm}^{-3}}$
(iv) Calculate the total number of moles of $\mathrm{L}_{2}$ in the two phases $\mathbf{A}$ and $\mathbf{B}$.

$$
K_{D}=3.64
$$

(04+01)

Total number of moles of $\mathrm{I}_{2}$

$$
\begin{aligned}
n_{I_{2}} & =0.04 \mathrm{~mol} \mathrm{dm} \\
& \\
& =1.02 \times 10^{-3} \mathrm{~mol}
\end{aligned}
$$

(b) The above experiment was repeated under the same conditions, that is, at the same temperalure. using the same amount of $\mathrm{I}_{2}$ and the same volunes, but with the addition of $\mathrm{I}^{-}$ions to phase A. The system was then horoughly shaken and allowed to reach cquilibrium. The volume of $0.005 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution required to titrate the $\mathrm{I}_{2}$ in a $5.00 \mathrm{~cm}^{3}$ sample of phase A was $41.00 \mathrm{~cm}^{3}$. The concentration of $I_{2}$ in phase $\mathbf{B}$ was then determined to be $0.030 \mathrm{~mol} \mathrm{dm}^{-3}$.
(i) Calculate the amount of $\mathrm{I}_{2}$ (moles) expected in $500 \mathrm{~cm}^{3}$ of phase A , based on the partition coefficient for the distribution of $\mathrm{I}_{2}$ between the phases A and $\mathbf{B}$.

Concentration of $l_{2}$ in phase $A$ (when excess $l^{-1}$ is added)
$\left[I_{2}\right]_{A}=\left[I_{2}\right]_{\mathrm{E}} / \mathrm{K}_{\mathrm{D}}$

$$
\begin{align*}
{\left[I_{2}\right]_{A} } & =\frac{0.030 \mathrm{~mol} \mathrm{dm}}{}{ }^{-3}  \tag{05}\\
& =8.64 \\
& =82 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-9}
\end{align*}
$$

The amount of $\mathrm{I}_{2}$ in $5.00 \mathrm{~cm}^{3}$ of phase $\mathrm{A}=\mathrm{n}$

$$
\begin{align*}
\mathrm{n} & =8.242 \times 10^{-3} \mathrm{~mol} \mathrm{dm}  \tag{02+01}\\
& \times 5.00 \times 10^{-3} \mathrm{dm}^{3} \\
& =4.121 \times 10^{-5} \mathrm{~mol}
\end{align*}
$$

(01+01)
(ii) Calculate the amount (moles) of $\mathrm{L}_{2}$ reacted with $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ in the above titration.

The amount of $\mathrm{I}_{2}$ in $5.00 \mathrm{~cm}^{3}$ of phase $A$, after the addition of iodide $=n^{\prime}$

$$
\begin{aligned}
\mathrm{n}^{\prime} & =0.005 \mathrm{~mol} \mathrm{dm}^{-3} \times 41.00 \times 10^{-3} \mathrm{dm}^{3} \times 0.5 \\
& =1.025 \times 10^{-4} \mathrm{~mol}\left\{\text { or } 1.03 \times 10^{-4} \mathrm{~mol}\right\rangle
\end{aligned}
$$

(iii) Considering the different iodine species present in phase $\mathbf{A}$. explain why the answers obtained in parts ( $b$ )(i) and ( $b$ )(ii) above are different.

When $I^{\prime}$ ions are added to the phase $A, I_{2}$ and $I^{-}$combine to form $\mathrm{I}_{3}{ }^{-}$.
When phase $A$ is titrated with $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}, \mathrm{I}_{2}$ released from $\mathrm{I}_{3}^{-}$is also reacted with $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$.
Therefore, $n^{\prime}>n$.
(c) Liquids $\mathbf{X}$ and $\mathbf{Y}$ fom an ideal solution obeying Raoult's law.


Initially only liquid $\mathbf{X}$ was introduced in to an evacuated rigid container as shown in the figure.
Maintaining the liquid level at $l$, the system was allowed to reach equilibrium at 400 K . Th pressure of the container was measured to be $3.00 \times 10^{4} \mathrm{~Pa}$. The volume of the vapour phas when the liquid level is at $I$ was $4.157 \mathrm{dm}^{3}$. Then liquid $\mathbf{Y}$ was introduced in to the containea mixed with liquid $X$ and the system was allowed to reach equilibrium at 400 K . The liquis level was maintained at $l$. The molar ratio of $\mathbf{X}: \mathbf{Y}$ in the liquid phase was found to be $1: 3$ The pressure of the container was measured to be $5.00 \times 10^{4} \mathrm{~Pa}$.
(i) What is the saturated vapour pressure of $\mathbf{X}$ at 400 K ?

Saturated vapour pressure of $X$ at $400 \mathrm{~K}=3.00 \times 10^{4} \mathrm{~Pa}$.
(04+01)
(ii) Calculate the mole fractions of $\mathbf{X}$ and $\mathbf{Y}$ in the liquid phase at equilibrium.

$$
\begin{aligned}
\text { Mole fraction of } X \text { in the liquid phase } & =\frac{1}{(1+3)} \\
& =\frac{1}{4} \text { or } 0.25 \\
\text { Mole fraction of } Y \text { in the liquid phase } & =\frac{3}{(1+3)} \\
& =\frac{3}{4} \text { or } 0.75
\end{aligned}
$$

(iii) Calculate the partial pressure of $\mathbf{X}$ at equilibrium after the addition of $\mathbf{Y}$.

$$
\text { At equilibrium, } \quad \begin{aligned}
\mathrm{P}_{\mathrm{x}} & =\mathrm{Px}^{0} \mathrm{X}_{\mathrm{A}} \\
& =0.25 \times 3.0 \times 10^{4} \mathrm{~Pa} \\
& =7.5 \times 10^{3} \mathrm{~Pa}
\end{aligned}
$$

(iv) Calculate the partial pressure of $\mathbf{Y}$ at equilibrium.

$$
\begin{align*}
P_{y} & =P_{\text {total }}-P_{x} \\
& =5.0 \times 10^{4} \mathrm{~Pa}-7.5 \times 10^{3} \mathrm{~Pa}  \tag{02+01}\\
& =4.25 \times 10^{4} \mathrm{~Pa} \tag{01+01}
\end{align*}
$$

(v) Calculate the saturated vapour pressure of $Y$.

Saturated vapour pressure of $Y, P_{y}^{0}=\frac{P_{y}}{X_{y}}$

$$
\begin{align*}
P_{y}^{0} & =\frac{4.25 \times 10^{4} P a}{0.75}  \tag{04+01}\\
& =5.67 \times 10^{4} \mathrm{~Pa}
\end{align*}
$$

(vi) Calculate the amounts (in moles) of $\mathbf{X}$ and $\mathbf{Y}$ in the vapour phase.

The amount of $X$ in the gas phase, $n_{x}=P_{x} V / R T^{\circ}$

$$
\begin{equation*}
n_{x}=\frac{7.5 \times 10^{3} \mathrm{~Pa} \times 4.157 \times 10^{-3} \mathrm{~m}^{3}}{8.314 \mathrm{~J} \mathrm{~mol}}{ }^{-1} \mathrm{~K}^{-1} \times 400 \mathrm{~K}, \tag{04+01}
\end{equation*}
$$

$$
\begin{equation*}
n_{x}=9.38 \times 10^{-3} \mathrm{~mol} \tag{04+01}
\end{equation*}
$$

Similarly,

$$
\begin{aligned}
n_{y} & =\frac{4.25 \times 10^{4} \mathrm{~Pa} \times 4.157 \times 10^{-3} \mathrm{~m}^{3}}{8.314 \mathrm{~J} \mathrm{~mol}} \\
n_{y} & =5.31 \times 10^{-2} \mathrm{~mol}
\end{aligned}
$$

(vii) When a mixture of the Jiquids $\mathbf{X}$ and $\mathbf{Y}$ is subjected to fractional distillation, state which compound would distill out first from the fractional distillation column. Give reason/s for your answer.

Compound Y can be obtained first.
Y is the more volatile compound or saturated vapour pressure of $\mathrm{Y}\left(\mathrm{P}^{0} \mathrm{y}\right)$ is high. Therefore, its vapour comes out first from the fractional distillation column.

Note :To award marks for (vil) answers for $\mathbf{P}_{x}{ }^{\circ}$ and $\mathbf{P}_{\gamma}{ }^{\circ}$ must have been calculated. Prediction must be according to the calculated $P_{x}{ }^{\circ}$ and $P_{y}{ }^{\circ}$ values.
$6(c)=70$ marks
7. (a) Using only the chemicals given in the list, show how you would carry out the following conversion

$$
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CHO} \rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COCH}_{3}
$$

List of chemicals
aqueous $\mathrm{NaOH}_{3}, \mathrm{HBr}$, alcoholic $\mathrm{KOH}, \mathrm{NaBH}_{4}, \quad \mathrm{H}^{+} / \mathrm{KMnO}_{4}$
Your conversion should not exceed 7 steps.

7 (a)


Note : Do not award 60 marks if there are more than seven steps. Do not award marks for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CHO}$ and $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COCH}_{3}$.

## Marking of partially correct answer

Mark from the beginning till an incorrect answer (reagent or product) is found. Mark from the end till an Incorrect answer (reagent or product) is found. Add the marks. Do not award marks for any isolated correct steps in the middle.
To award marks for reagent, both reactant and product have to be correct.
(b) Identify $\mathbf{R}_{1}-\mathbf{R}_{4}$ and $\mathbf{X}_{1}-\mathbf{X}_{4}$ and $\mathbf{Y}_{1}, \mathbf{Y}_{2}$ in order to complete the following reaction scherne

(1) Na (OH
(2) $\mathrm{H}^{+}$


```
\(X_{1}=\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}\)
\[
\begin{equation*}
\mathrm{X}_{2}=\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{OH} \tag{06}
\end{equation*}
\]
\[
\begin{equation*}
\mathrm{X}_{3}=\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CHO} \tag{06}
\end{equation*}
\]




```

$\mathbf{R}_{4}=$ 1. $\mathrm{LiAlH}_{4}$ 2. $\mathrm{H}_{2} \mathrm{O}$ OR $\mathrm{H}_{2} \mathrm{O} / \mathrm{H}^{+}$
$\mathrm{R}_{\mathbf{2}}=\mathrm{PCC}$
$\mathbf{R}_{3}=\mathrm{FeCl}_{3} / \mathrm{Cl}_{2}$ OR $\mathrm{Fe} / \mathrm{Cl}_{2}$ OR Lewis acld $/ \mathrm{Cl}_{2}$
$\mathrm{R}_{4}=$ 1. NaOH 2. $\mathrm{H}_{2} / \mathrm{Pd} / \mathrm{BaSO}_{4} /$ quinoline $\quad \mathrm{OR}$

1. NaOH 2. Lindlar/ $\mathrm{H}_{2}$
```
(Note : NsOH is not required for award of 06 marks ) \(\quad(06\) marks \(\mathbf{x} 10=06\) )
\(7(b)=60\) marks

\section*{Alternative Pathway}




\(\mathrm{Y}_{2}=\mathrm{H}_{2} \mathrm{~N}-\square-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}_{3}\)
OR

\(\mathrm{R}_{1}=\mathrm{FeCl} 3_{3} / \mathrm{Cl}_{2}\) OR \(\mathrm{Fe} / \mathrm{Cl}_{2}\) OR Lewis acid/ \(/ \mathrm{Cl}_{2}\)
\(\mathbf{R}_{2}=\) 1. \(\mathrm{LiAlH}_{4}\) 2. \(\mathrm{H}_{2} \mathrm{O}\) OR \(\mathrm{H}_{2} \mathrm{O} / \mathrm{H}^{+}\)
\(\mathrm{R}_{3}=\mathrm{PCC}\)
\(\mathrm{R}_{4}=\begin{aligned} & \text { 1. } \mathrm{NaOH} 2 \mathrm{H}_{2} / \mathrm{Pd} / \mathrm{BaSO} / \text { /quinoline } \quad \mathrm{OR} \\ & \\ & \\ & \\ & \text { 1. } \mathrm{NaOH} \\ & \text { (Note : } \mathrm{NaOH} \text { is not required for award of } 06 \text { marks ) }\end{aligned}\)
( 06 marks \(\times 10=60\) )
\[
7(b)=60 \text { marks }
\]
(c) (i) Give the mechanism of the following reaction.
\[
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}+\mathrm{HBr} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Br}+\mathrm{H}_{2} \mathrm{O}
\]


Note: At least one lone pair should be given.
(02)

(ii) State whether the above reaction is a nucleophilic substitution reaction or an electrophilic substintion reaction. Identify the nucleophile or electrophile as appropriate.
(ii) Nucleophilic substitution, \(\mathrm{Br}^{\ominus}\)
(iii) State giving reasons which of the two compounds, phenol ( \(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}\) ) or ethanol ( \(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\) )
\[
\begin{array}{r}
\text { is more acidic. } \\
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{O}^{\ominus}+\mathrm{H}_{3}{ }^{\oplus} \\
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{\ominus}+\mathrm{H}_{3}{ }^{\oplus} \tag{02}
\end{array}
\]

Note: If \(\mathrm{H}_{2} \mathrm{O}\) is not included in the equations, only (01) per equation
- In the above equilibria the equilibrium point for phenol is more toward the right than ethanol.
- This is because the stability of phenate ion relative to phenol is greater than the stability of the alkoxide relative to alcohol.
- The phenate ion is more stable because its negative charge gets delocalized by resonance.
- Resonance structures drawn
- In alkoxide ion there is no such charge dispersion/ No resonance
- Phenol is more acidic than ethanol.

PART C - ESSAY
Answer two questions only. (Each question carries 15 marks.)
8. (a) An aqueous solution \(P\) contains two cations and two anions. The following experiments were canied out to identify these cations and anions.
Cations
\begin{tabular}{|c|c|c|}
\hline & Experiment & Observation \\
\hline (1) & \(\mathbf{P}\) was acidified with dilute HCl and \(\mathrm{H}_{2} \mathrm{~S}\) was bubbled through the solution. & A clear solution was obtained. \\
\hline (2) & The above solution was boiled till all the \(\mathrm{H}_{2} \mathrm{~S}\) was removed, A few drops of conc- \(\mathrm{HNO}_{3}\) were added and the solution was heated further. The resulting solution was cooled and \(\mathrm{NH}_{4} \mathrm{Cl} / \mathrm{NH}_{4} \mathrm{OH}\) was added. & A brown precipitate (Q) was formed. \\
\hline (3) & Q was removed by filtration and \(\mathrm{H}_{2} \mathrm{~S}\) was bubbled through the filtrate. & A pale pink precipitate ( \(\mathbf{R}\) ) was formed. \\
\hline (4) & \(\mathbf{R}\) was removed by filtration and the filtrate was boiled till all the \(\mathrm{H}_{3} \mathrm{~S}\) was removed. \(\left(\mathrm{NH}_{4}\right)_{2} \mathrm{CO}_{3}\) was added to the solution. & A clear solution was obtained, \\
\hline (5) & Dilute NaOH was added to a fresh portion of \(\mathbf{P}\). & A dirty-green precipitate and a while precipitate were formed. \\
\hline
\end{tabular}

Experiments for precipitates \(\mathbf{Q}\) and \(\mathbf{R}\) :
\begin{tabular}{|l|l|}
\hline \multicolumn{1}{|c|}{ Experiment } & \multicolumn{1}{|c|}{ Observation } \\
\hline \begin{tabular}{l} 
Q was dissolved in dil. \(\mathrm{HNO}_{3}\) and a salicylic acid solution \\
was added.
\end{tabular} & \begin{tabular}{l} 
A light purple solution was \\
obtained.
\end{tabular} \\
\hline \(\mathbf{R}\) was dissolved in dilute acid and dil. NaOH was added \\
to the solution. & \begin{tabular}{l} 
A white precipitate was formed. \\
It tumed brown on standing.
\end{tabular} \\
\hline
\end{tabular}

\section*{Anions}

(i) Identify the two cations and the two anions in solution P. (Reasons are not required.)
\[
\begin{array}{lll}
\text { Cations: } & \mathrm{Fe}^{2+} \text { and } \mathrm{Mn}^{2+} & (10+10) \\
\text { Anions: } & \mathrm{SO}_{4}^{2-} \text { and } \mathrm{Br} & (08+07)
\end{array}
\]

Note: First correct anion (08), second anion (07)
(ii) Write the chemical fomulae of the precipitates \(\mathbf{Q}\) and \(\mathbf{R}\).

Q- \(\quad \mathrm{Fe}(\mathrm{OH})_{3}\)
R-MnS
(iii) Give reasons for the following:
I. Removal of \(\mathrm{H}_{7} \mathrm{~S}\) in experiment (2) for cations.
- If \(\mathrm{H}_{2} \mathrm{~S}\) is not removed \(\mathrm{Mn5} / \mathrm{FeS} /\) cations of group IV will also precipitate when \(\mathrm{NH}_{4} \mathrm{OH} / \mathrm{NH}_{4} \mathrm{Cl}\) solution is added. OR
- \(\mathrm{H}_{2} \mathrm{~S}\) can be oxidized to sulphur by conc. \(\mathrm{HNO}_{3}\).
- A fine precipitate of sulphur would be formed in solution if \(\mathrm{H}_{2} \mathrm{~S}\) is not removed.
II. Heating with conc. \(\mathrm{HNO}_{3}\) in experiment for cations.
- \(\mathrm{K}_{\mathrm{sp}}\) of \(\mathrm{Fe}(\mathrm{OH})_{2}>\mathrm{K}_{\mathrm{sp}}\) of \(\mathrm{Fe}(\mathrm{OH})_{3}\)
- Therefore, \(\mathrm{Fe}^{2+}\) needs to be converted to \(\mathrm{Fe}^{3+}\) to be completely precipitated.
OR
- Conc. \(\mathrm{HNO}_{3}\) must be added to oxidize iron if present, to the ferric state.
- If originally present, it would have been reduced by the \(\mathrm{H}_{2} \mathrm{~S}\) to the ferrous ion.
- Ferrous ion is not completely precipitated by \(\mathrm{NH}_{4} \mathrm{OH} / \mathrm{NH}_{4} \mathrm{Cl}\) solution. (will get a mixture of \(\mathrm{Fe}^{2+}\) and \(\mathrm{Fe}^{3+}\) )
(b) The sample \(\mathbf{X}\) contains lead, copper and an inert matcrial. The following procedure was carried out to analyse lead and copper in \(\mathbf{X}\).

\section*{Procedure:}

A mass of 0.28 .5 g of X was dissolved in a slight excess of dil. \(\mathrm{HNO}_{3}\), A clear solution was obtained. A NaCl solution was added to the resulting clear solution. A white precipitate (Y) was formed. The precipitate was separated by filtration and the precipitate ( \(\mathbf{Y}\) ) and filtrate ( \(Z\) ) were analysed separately.

\section*{Precipitate ( \(\mathbf{Y}\) )}

The precipitate was dissolved in hot water. A solution of \(\mathrm{K}_{2} \mathrm{CrO}_{4}\) was added in excess. A yellow precipitate was formed. The precipitate was separated by filtration and dissolved in dil. \(\mathrm{HNO}_{3}\), An orange coloured solution was obtained. Excess KI was added to this solution and the liberated \(\mathrm{I}_{2}\) was tirrated with \(0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\), with starch as the indicator. The volume of \(\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\) required to reach the end point was \(27.00 \mathrm{~cm}^{3}\). (Assume that the \(\mathrm{NO}_{3}^{-}\)ions do not interfere with the titration.)

\section*{Filtrate ( \(Z\) )}

The filtrate was neutralized and excess KI was added to it. The liberated \(\mathrm{I}_{2}\) was titrated with \(0.100 \mathrm{~mol} \mathrm{dm} \mathrm{m}^{-3} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\), with starch as the indicator, The volume of \(\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\) required to reach the end point was \(15.00 \mathrm{~cm}^{3}\).
(Note: Assume that the inert material was soluble in dil. \(\mathrm{HNO}_{3}\) and did not interfere with the experiment)
(i) Calculate the mass percentages of lead and copper in \(\mathbf{X}\). Write balanced chemical equations where relevant.

\section*{Determination of Cu}
\[
\begin{align*}
& 2 \mathrm{Cu}^{2+}+4 \mathrm{l}^{-} \rightarrow \mathrm{I}_{2}+2 \mathrm{CuI} \\
& \mathrm{OR}_{2} \\
& 2 \mathrm{Cu}^{2+}+2 \mathrm{I}^{-} \rightarrow 2 \mathrm{Cu}^{+}+\mathrm{I}_{2}  \tag{1}\\
& \mathrm{I}_{2}+2 \mathrm{~S}_{2} \mathrm{O}_{3}^{2-} \rightarrow 2 \mathrm{l}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}^{2-} \tag{2}
\end{align*}
\]
------------(1)
\[
\begin{align*}
& =\frac{0.10}{1000} \times 15.0  \tag{03}\\
& =\frac{0.10}{1000} \times 15.0  \tag{03}\\
& =\frac{0.10}{1000} \times 15.0 \times 63.5  \tag{03}\\
& =0.095 \mathrm{~g}
\end{align*}
\]

Therefore, moles of \(\mathrm{Cu}^{2+}\)
Mass of Cu
\(=\frac{0.095}{0.285} \times 100\)
= \(33.4 \%\)

\section*{Determination of \(\mathbf{P b}\)}
\[
\begin{equation*}
\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+6 \mathrm{l}^{-}+14 \mathrm{H}^{+} \rightarrow 2 \mathrm{Cr}^{3+}+3 \mathrm{I}_{2}+7 \mathrm{H}_{2} \mathrm{O} \tag{3}
\end{equation*}
\]
\(\mathrm{I}_{2}+2 \mathrm{~S}_{2} \mathrm{O}^{2}{ }^{2} \rightarrow 2 \mathrm{I}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}{ }^{2-}\)
From (3) \(+3 \times(4) \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}=6 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2}\)-OR Identification of correct stoichiometry
Moles of \(\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-} \quad=\frac{0.10}{1000} \times 27.0\)
Moles of \(\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-} \quad=\frac{1}{6} \times \frac{0.10}{1000} \times 27.0\)
\(2 \mathrm{CrO}_{4}{ }^{2-}+2 \mathrm{H}^{+} \rightarrow \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}+\mathrm{H}_{2} \mathrm{O}\)

Therefore, moles of Cr
\[
\begin{equation*}
=2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0 \tag{03}
\end{equation*}
\]

Yellow precipitate is \(\mathrm{PbCrO}_{4}\)
Therefore, moles of Pb
\[
\begin{equation*}
=2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0 \tag{03}
\end{equation*}
\]

Therefore, mass of Pb
\[
\begin{equation*}
=2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0 \times 207 \tag{03}
\end{equation*}
\]
\[
\begin{equation*}
=0.186 \mathrm{~g} \tag{03}
\end{equation*}
\]

Therefore, \%Pb
\[
\begin{equation*}
=\frac{0.186}{0.285} \times 100 \tag{03}
\end{equation*}
\]
\[
=65.3 \%
\]

\section*{Alternate method}

\section*{Determination of Pb}
\[
\begin{align*}
& 2 \mathrm{CrO}_{4}^{2-}+6 \mathrm{I}^{-}+16 \mathrm{H}^{+} \rightarrow 2 \mathrm{Cr}^{3+}+3 \mathrm{I}_{2}+4 \mathrm{H}_{2} \mathrm{O}  \tag{3}\\
& \mathrm{I}_{2}+2 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-} \rightarrow 2 \mathrm{I}^{-}+\mathrm{S}_{4} \mathrm{O}_{6}^{2-} \tag{4}
\end{align*}
\]

OR
\[
\begin{aligned}
& \mathrm{CrO}_{4}{ }^{2-}+8 \mathrm{H}^{+}+3 \mathrm{e} \rightarrow \mathrm{Cr}^{3+}+4 \mathrm{H}_{2} \mathrm{O} \\
& 2 \mathrm{I}^{-} \rightarrow \mathrm{I}_{2}+2 \mathrm{e}
\end{aligned}
\]

From equations \(\mathrm{CrO}_{4}{ }^{2-}=3 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}\) OR Identification of correct stoichiometry
Moles of \(\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\)
\[
\begin{equation*}
=\frac{0.10}{1000} \times 27.0 \tag{03}
\end{equation*}
\]

Moles of \(\mathrm{I}_{2}\)
\(=\frac{1}{2} \times \frac{0.10}{1000} \times 27.0\)
\(=\frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0\)
\(=9 \times 10^{-4}\)
Therefore, moles of \(\mathrm{PbCrO}_{4} \quad=\frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0=9 \times 10^{-4}\)
Moles of \(\mathrm{Cr}^{3+}\)

Therefore, moles of Pb
\(=\frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0=9 \times 10^{-4}\)
Therefore, mass of Pb
\(=9 \times 10^{-4} \times 207 \mathrm{~g}\)
- \(\times 10^{4} \times 207\)
\(=0.186 \mathrm{~g}\)
\(=\frac{0.186}{0.285} \times 100\)
\(=65.3 \%\)
(ii) What is the colour change at the end point in the titration carried out in the analysis of precipitate \(\mathbf{Y}\) ?
\((\mathrm{Cu}=63.5, \mathrm{~Pb}=207)\)
Blue \(\rightarrow\) Green
9. (a) The following questions are based on the environment and related issues.
(i) Identify three greenhouse gases that contribute to global warming. State two consequences of global warming.

Greenhouse gases that contribute to global warming.
\(\mathrm{CO}_{2}, \mathrm{NO}_{x}, \mathrm{~N}_{2} \mathrm{O}, \mathrm{O}_{3}, \mathrm{CFC}\), methane, volatile hydrocarbons (03+03+03)

\section*{Consequences:}
- Melting of polar ice caps
- Change in weather patterns
- Drying up of freshwater reservoirs
- Sinking of low lying countries due to thermal expansion of sea water/ sea level rise
- desertification
- loss of soil moisture
- changes in biodiversity
- decrease in dissolved oxygen content
- increase in populations of certain insects
(Any two)
(ii) Global environmental issues caused by coal power plants are well known. Identify one such issue that contributes significantly to change in certain water quality parameters in rivers and lakes.

> Acid rain
(iii) Name the chernical species responsible for the environmental issue identified in (ii) above and state three water quality parameters that are likely to be affected by this issue.
\[
\begin{equation*}
\mathrm{SO}_{2} / \mathrm{SO}_{3} / \mathrm{H}_{2} \mathrm{SO}_{3} / \mathrm{H}_{2} \mathrm{SO}_{4} \tag{03}
\end{equation*}
\]

Water parameters affected:
- pH (decreases) / acidity (increases)
- Salinity (increases)
- Concentration of heavy metals (increases)
- Hardness (increases)
- Conductivity (increases)
(Any three)
\[
(03+03+03)
\]
(iv) Identify two envirommental issues that change (increase or decreasc) the ozone level in the atmosphere and explain briefly how these changes take place with the aid of balanced cherrical equations.
\[
\begin{align*}
& \text { photochemical smog (Ozone increases) } \\
& \text { How } \\
& \text { Vehicle emissions contain } \mathrm{NO}_{x} \\
& \text { ( } \mathrm{M}=\text { third body) }  \tag{03}\\
& \text { ozone layer depletion (Ozone decreases) } \\
& \text { How } \\
& \text { Ozone destroyed by free radicals }(\dot{\mathrm{X}})(\mathrm{e} . \dot{\mathrm{H}}, \stackrel{\mathrm{NO}}{\mathbf{O}}, \dot{\mathrm{O}}, \dot{\mathrm{C}} \text { ) } \\
& \text { which act as a catalyst. }  \tag{03}\\
& \text { (1) } \mathrm{x} 2+(2)+(3) \mathrm{x} 2  \tag{03}\\
& 2 \mathrm{O}_{3}(\mathrm{~g}) \quad \longrightarrow 3 \mathrm{O}_{2}(\mathrm{~g}) \tag{03}
\end{align*}
\]
(v) I. "Most of the harmful gases in vehicle exhausts are converted to relatively harmless gases by catalycic converers." Briefly explain this statement.

Catalytic converters convert
- \(\mathrm{NO}(\mathrm{g})\) formed to \(\mathrm{N}_{2}(\mathrm{~g})\)
- \(\mathrm{CO}(\mathrm{g})\) formed to \(\mathrm{CO}_{2}(\mathrm{~g})\)
- Unburnt or partially burnt hydrocarbons to \(\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g})\)
II. Name the harmful gas (except \(\mathrm{CO}_{2}\) ) that is not converted to a less harmful gas by the calalytic converter. State briefly how this harmful gas is formed in the vehicle engine.
\[
\mathrm{SO}_{2}
\]

Certain fossil fuels contain sulphur.
Burning of sulphur produces \(\mathrm{SO}_{2}\).
(vii) Give balanced chemical equations wilh appropriate conditions, for reactions taking place in \(\mathbf{M}_{1}, \mathbf{M}_{2}\) and \(\mathbf{M}_{3}\).
\[
\begin{align*}
& \mathbf{M}_{1}: \quad \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \stackrel{(200-250) \mathrm{atm}}{\rightleftharpoons} \stackrel{(01)}{\rightleftharpoons} 2 \mathrm{NH}_{3}(\mathrm{~g})  \tag{02}\\
& \text { (400-450) }{ }^{\circ} \mathrm{C}(\mathbf{0 1 )} \\
& \mathrm{Fe} \text { (catalyst) (01) } \\
& \mathrm{K}_{2} \mathrm{O} \text { and } \mathrm{Al}_{2} \mathrm{O}_{3} \text { (promoters) (01) }
\end{align*}
\]
\[
\begin{align*}
& 2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \xrightarrow{150^{\circ} \mathrm{C}(01)} 2 \mathrm{NO}_{2}  \tag{02}\\
& 4 \mathrm{NO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 4 \mathrm{HNO}_{3}(\mathrm{aq}) \tag{02}
\end{align*}
\]

Note: Physical states are not required.
(viii) I. Give one use of each compound \(\mathbf{P}_{\mathbf{1}}\) and \(\mathbf{P}_{\mathbf{2}}\) other than those mentioned above.

\section*{\(P_{1}\) :}
- Neutralizing acidic constituents in industry / emissions/ effluents / water treatment plants
- In stack emission control systems to neutralize sulphur oxides from combustion of sulphur-containing fuels
- As a refrigerant
- In the rubber industry / for the stabilization of natural and/or synthetic latex / to prevent premature coagulation
- In the paint industry
(Any one)

\section*{\(P_{2}\) :}
- To manufacture nitrates OR
\(\mathrm{NaNO}_{3}\) - meat preservative OR
\(\mathrm{AgNO}_{3}\) - prepare photographic films and paper
- For the preparation of aqua regia
- Used to clean soldering surfaces
(Any one)
I. Give one use of \(\mathbf{R}_{1}\) in the manufacturing process \(\mathbf{P}_{1}\) other than being used as a raw material.

As a fuel \(O R \quad\) to heat the system (to \(450^{\circ} \mathrm{C}\) )

\section*{9(b): 75 marks}
10. (a) A and \(\mathbf{B}\) are complex ions, (i.e. metal ion and ligands coordinated to it) with an octahedral geometry. They have the same atomic composition of \(\mathrm{MnC}_{5} \mathrm{H}_{3} \mathrm{~N}_{6}\). In each complex ion, two types of ligands are coordinated to the metal ion. When an aqueous solution containing A is treated with a potassium salt, the coordination compound C is formed. \(\mathbf{C}\) gives four ions in aqueous solution. When an aqueous solution containing \(\mathbf{B}\) is treated with a potassium salt the coordination compound \(\mathbf{D}\) is formed. \(\mathbf{D}\) gives three ions in aqueous solution. Both C and D have an octahedral geometry.
(Note: The oxidation states of manganese in \(\mathbf{A}\) and \(\mathbf{B}\) do not change on treatment with the potassium salt).
(i) Identify the ligands coordinated to manganese in \(\mathbf{A}\) and \(\mathbf{B}\).
\[
\begin{equation*}
\mathrm{CN}^{-} \text {and } \mathrm{NH}_{3} \tag{05+05}
\end{equation*}
\]
(ii) Give the structures of \(\mathbf{A}, \mathbf{B}, \mathbf{C}\) and \(\mathbf{D}\).
\begin{tabular}{lll} 
A: \(:\left[\mathrm{Mn}(\mathrm{CN})_{5}\left(\mathrm{NH}_{3}\right)\right]^{3-}\) & OR & {\(\left[\mathrm{Mn}\left(\mathrm{NH}_{3}\right)(\mathrm{CN})_{5}\right]^{3-}\)} \\
B: \(\left[\mathrm{Mn}(\mathrm{CN})_{5}\left(\mathrm{NH}_{3}\right)\right]^{2-}\) & OR & {\(\left[\mathrm{Mn}\left(\mathrm{NH}_{3}\right)(\mathrm{CN})_{5}\right]^{2-}\)} \\
C:K \(\mathrm{K}_{3}\left[\mathrm{Mn}(\mathrm{CN})_{5}\left(\mathrm{NH}_{3}\right)\right]\) & OR & \(\mathrm{K}_{3}\left[\mathrm{Mn}\left(\mathrm{NH}_{3}\right)(\mathrm{CN})_{5}\right]\) \\
\(\mathrm{D}: \mathrm{K}_{2}\left[\mathrm{Mn}(\mathrm{CN})_{5}\left(\mathrm{NH}_{3}\right)\right]\) & OR & \(\mathrm{K}_{2}\left[\mathrm{Mn}\left(\mathrm{NH}_{3}\right)(\mathrm{CN})_{5}\right]\)
\end{tabular}
(iii) Write the electronic configurations of the manganese ions in \(\mathbf{A}\) and \(\mathbf{B}\).

A, oxidation state of \(\mathrm{Mn}=+2\)
Therefore, electronic configuration of Mn in A is, \(1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 3 d^{5}\)

B, oxidation state of \(\mathrm{Mn}=+3\)
Therefore, electronic configuration of Mn in \(\mathbf{B}\) is, \(\quad 1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 3 d^{4}\)
(iv) Write the IUPAC names of \(\mathbf{C}\) and D .

C potassium amminepentacyanidomanganate(II)
D potassium amminepentacyanidomanganate(III)
Note : If spelling is incorrect do not award marks.
10(a): 75 marks
(b) (i) I. Write the reduction half reaction corresponding to the electrode, \(\mathrm{Ag}(\mathrm{s})|\mathrm{AgCl}(\mathrm{s})| \mathrm{Cl}(\mathrm{aq})\).
\[
\begin{equation*}
\mathrm{AgCl}(\mathrm{~s})+\mathrm{e} \longrightarrow \mathrm{Ag}(\mathrm{~s})+\mathrm{Cl}(\mathrm{aq}) \tag{05}
\end{equation*}
\]
\((\rightleftharpoons\) accepted). Physical states are required.
II. State whether the electrode potential of \(\mathrm{Ag}(\mathrm{s})|\mathrm{AgCl}(\mathrm{s})| \mathrm{Cl}^{-}(\mathrm{aq})\) depends on the \(\mathrm{Ag}^{+}\) concentration in the solution. Explain your answer.

No.
\(\mathrm{Ag}^{+}(\mathrm{aq})\) does not appear in the electrode reaction (half reaction).
(ii) Consider the following reaction.
\[
\mathrm{Fe}(\mathrm{~s})+2 \mathrm{H}^{+}(\mathrm{aq})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
\]
I. Write the oxidation and reduction half reactions relevant to the above reaction.
\(\mathrm{Fe}(\mathrm{s}) \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{e} \quad\) (oxidation half reaction)
\(1 / 2 \mathrm{O}_{2}(\mathrm{~g})+2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{e} \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})\) (reduction half reaction)
\((\Longrightarrow\) accepted) Physical states are required.
iI. Given that the above reaction is the cell reaction of an electrochemical cell, determine the standard electromotive force of the cell.
\[
\begin{array}{rlrl}
\mathrm{E}_{\mathrm{Fe}^{2+}(\mathrm{aq}) / \mathrm{Fe}(\mathrm{~s})}^{0}=-0.44 \mathrm{~V} & \mathrm{E}_{\mathrm{H}^{+}(\mathrm{aq}) / \mathrm{o}_{2}(\mathrm{~g}) / \mathrm{H}_{2} \mathrm{O}(\mathrm{l})}^{\mathrm{o}}=1.23 \mathrm{~V} \\
\text { Standard cell potential } & =1.23 \mathrm{~V}-(-0.44 \mathrm{~V}) \\
& =1.67 \mathrm{~V} & (1.23-(-0.44)) \mathrm{V} & (01+01)+(01+01)
\end{array}
\]
(iii) A conslant current of 100 mA was passed through \(100.00 \mathrm{~cm}^{3}\) of a \(0.10 \mathrm{~mol}^{-3} \mathrm{~m}^{-3}\) aqueous \(\mathrm{CaBr}_{2}\) solution as shown in the diagram. The temperature of the system was maintained at \(25^{\circ} \mathrm{C}\).

I. Write the oxidation and reduction reactions that take place at the electrodes.

Oxidation half reaction,
\(2 \mathrm{Br}_{2}(\mathrm{aq}) \longrightarrow \mathrm{Br}_{2}(\mathrm{~g})+2 \mathrm{e} \quad \mathrm{OR} \quad 2 \mathrm{Br}^{-}(\mathrm{aq}) \longrightarrow \mathrm{Br}_{2}(\mathrm{l})+2 \mathrm{e}\)
Reduction half reaction,
\(2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+2 \mathrm{e} \longrightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq})\)
( \(=\) accepted). Physical states are required.
II. Calculate the time taken for the commencement of precipitation of \(\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})\). Solubility product of \(\mathrm{Ca}(\mathrm{OH})_{2}\) at \(25^{\circ} \mathrm{C}\) is \(1.0 \times 10^{-5} \mathrm{~mol}^{3} \mathrm{dm}^{-9}\). Neglect the ionization of water. Assume that the volume of the aqueous phase remains constant.
\(\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})^{2}\right]^{2}\)
Required concentration of \(\mathrm{OH}^{-}\)to start precipitation of \(\mathrm{Ca}(\mathrm{OH})_{2}=\left[\mathrm{OH}^{-}\right]\)
\[
\left[O H^{-}\right]=\sqrt{\frac{1.0 \times 10^{-5} \mathrm{~mol}^{3} \mathrm{dm}^{-9}}{0.1 \mathrm{~mol} \mathrm{dm}^{-3}}} \quad \text { OR } \quad 1.0 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}
\]

The amount of \(\mathrm{OH}^{-}\)required to provide the above concentration \(=\)nor- \(^{\text {or }}\)
\(n_{\text {OH }}=1.0 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \times 100 \times 10^{-3} \mathrm{dm}^{3}\) OR \(1.0 \times 10^{-3} \mathrm{~mol}\)
Amount of charge, that must be passed through the solution, \(Q\),
\(\mathrm{Q}=1.0 \times 10^{-3} \mathrm{~mol} \times 96500 \mathrm{C} \mathrm{mol}^{-1}\) OR 96.5 C
(04+01)
Time required to pass the charge \(Q\), when the current flow is \(100 \mathrm{~mA}, \mathrm{t}\)
\(t=\frac{96.5 \mathrm{C}}{100 \times 10^{-3} \mathrm{Cs}^{-1}}\) OR 965 s OR 16.08 min
(For the Faraday constant, a value between \(96500 \pm 100 \mathrm{C} \mathrm{mol}^{-1}\) is accepted, If the symbol \(F\) is used for the Faraday constant, and \(t\) is calculated using \(F\), full marks can be awarded. \(\mathrm{t}=16.08 \mathrm{~min}\) OR \(\mathrm{t}=16 \mathrm{~min}\) accepted.)```

