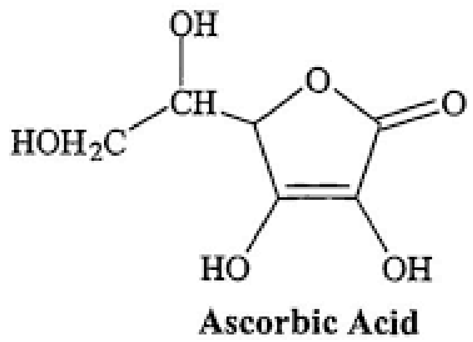
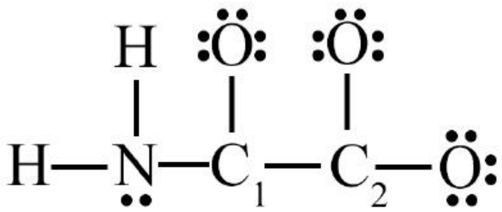
மொறட்டுவைப் பல்கலைக்கழக பொறியியற் பீட தமிழ் மாணவர்கள் நடாத்தும் க.பொ.த உயர்தர மாணவர்களுக்கான 9வது

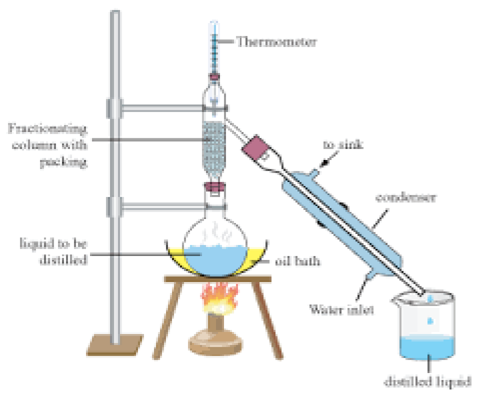
முன்னோடிப் பரீட்சை – 2018

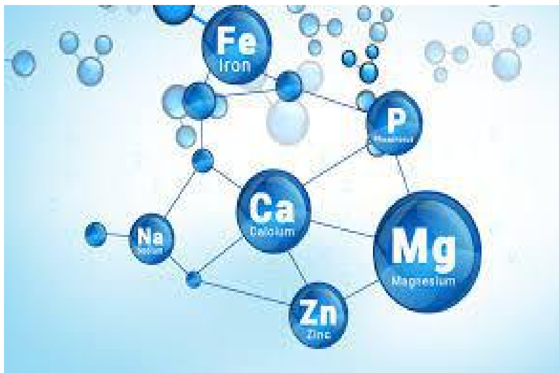
02 - இரசாயனவியல் விடைகள்

(ஆங்கில மொழி மூலமானது)









Prepared By

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Brown road, Jaffna.

மொறட்டுவை பல்கலைக்கழக பொறியியற் பீட தமிழ் மாணவர்கள்

நடாத்தும் க.பொ.த உயர்தர மாணவர்களுக்கான 9வது

முன்னோடிப் பரீட்சை – 2018

பாடஎண் } 02 பாடம் } இரசாயனவியல்

வினா இல.	விடை இல.	வினா இல.	விடை இல.	வினா இல.	விடை இல.	வினா இல.	விடை இல.	வினா இல.	விடை இல.
01)	3	11)	1	21)	3	31)	5	41)	3
02)	2	12)	5	22)	1	32)	3	42)	5
03)	5	13)	3	23)	2	33)	2	43)	4
04)	1	14)	2	24)	5	34)	5	44)	3
05)	2	15)	2	25)	3	35)	4	45)	2
06)	5	16)	3	26)	2	36)	4	46)	1
07)	4	17)	4	27)	1	37)	2	47)	2
08)	3	18)	3	28)	4	38)	1	48)	1/4
09)	1	19)	2	29)	3	39)	5	49)	1
10)	4	20)	5	30)	1	40)	5	50)	4

விசேட அறிவுறுத்தல் } ஒரு சரியான விடைக்கு 01 புள்ளி வீதம் 50

மொத்தப் புள்ளிகள் 1 X 50 = 50

Part A – Structured Essay

Answer **all four** questions on this paper it self

(Each question carries **10** marks)

Do not write anything here.

1. (a) Arrange the following in the **increasing** order of the property indicated in parenthesis.

i. C, Li, Si (electron affinity)

Li < **C** < **Si**

ii. N_2H_4, $NaNH_2$, NH_2OH (oxidation state of N atom)

$NaNH_2$ < **N_2H_4** < **NH_2OH**

iii. Li^+, Cl^-, Al^{3+} (Hydration energy)

Cl^- < **Li^+** < **Al^{3+}**

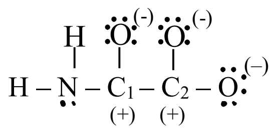
iv. $KHCO_3$, $NaHCO_3$, $Mg(HCO_3)_2$ (Decomposition temperature)

$Mg(HCO_3)_2$ < **$NaHCO_3$** < **$KHCO_3$**

v. $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ (Solubility)

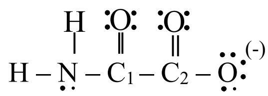
$Mg(OH)_2$ < **$Ca(OH)_2$** < **$Sr(OH)_2$**

(b) The compound with the molecular formula $H_3C_2NO_3$ reacts with NaOH $_{(aq)}$ solution and gives a compound with the molecular formula $H_2C_2NO_3Na$ and water as the products. Answer the following questions which are based on the anion of this sodium salt. The **first step** of the Lewis structure of anion is given below,

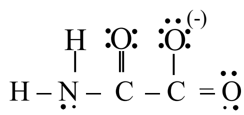


i. Mark the appropriate formal charges of carbon and oxygen atoms in the above structure.

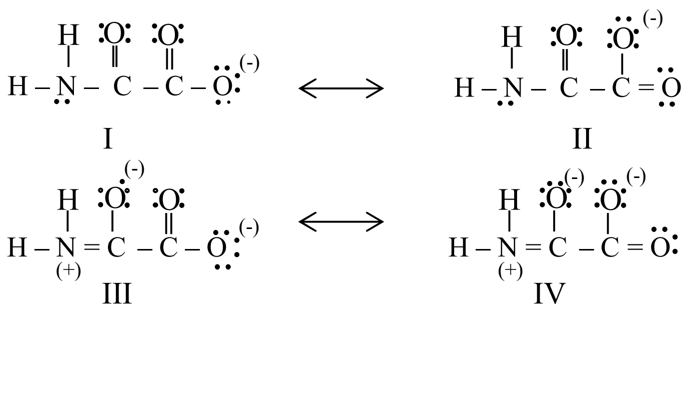
ii. Draw the **most acceptable** Lewis structure for this anion.



OR



iii. Draw all the possible resonance structures for this anion.



[See page 4

Do not write anything here.

iv. Giving reasons, comment on their relative stabilities of the resonance structures drawn in part (iii) above.

Resonance structures I, II are relatively stable. And both of them are equally stable.

Charge distribution is less, and O atom carries negative (-) charge.

Resonance structures III, IV are relatively least stable. And both of them are equally stable. Charge distribution is high and electronegative atom N carries positive (+) charge.

v. State the followings regarding the C and N atoms, given in the table below.

1. VSEPR pairs around the atom
2. electron pair geometry (arrangement of electron pairs) around the atom
3. shape around the atom
4. hybridization of the atom

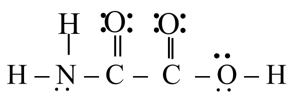
		C_1	C_2	N
ρ8	VSEPR pairs	**3**	**3**	**4**
ς8	electron pair geometry	**Trigonal planer**	**Trigonal planer**	**Tetrahedral**
σ8	shape	**Trigonal planer**	**Trigonal planer**	**Trigonal pyramidal**
τ8	hybridization	**sp^2**	**sp^2**	**sp^3**

vi. Identify the atomic/ hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure drawn in part (ii) above.

1. C_1–C_2 **C, sp^2(h.o) – C_2, sp^2(h.o)**
2. C_1 – N **C_1, sp^2(h.o) – N, Sp^3 (h.o)**
3. N – H **N, sp^3 (h.o) – H_1S(a.o)**
4. C_1 – O **C_1Sp^2(h.o) – O, 2p 2p(a.o)**

vii. When dil HCl is added to the above anion, a compound with molecular formula $H_3C_2NO_3$ is obtained.

1. Draw the structure obtained, by considering whether H^+ ion joins with oxygen atom / nitrogen atom.



2. By considering the atom in which H^+ ion is joined, underline the suitable phrase.

State of Hybridization (changes/ does not change)
Oxidation state (increases/ decreases/ does not change)
Charge (increases/ decreases/ does not change)
Number of VSEPR pairs (increases/ decreases/ does not change)
Electronegativity (increases/ decreases/ does not change)

(c) Among the following molecules which one /ones will have the following intermolecular attractive forces.

$CS_{2(l)}$, $CH_2Cl_{2(l)}$, $NH_2OH_{(l)}$, $XeO_{3(l)}$, $C_6H_{6(l)}$

i. hydrogen bond

NH_2OH(l)

ii. dipole – dipole interaction

CH_2Cl_2(l), XeO_3(l)

iii. london dispersion forces.

CS_2(l), CH_2Cl_2(l), NH_2OH(l), XeO_3(l), C_6H_6(l)

Do not write anything here.

02.(a) A third period element "A" reacts with water and gives a solution B and gas molecules C, where C is a molecule of an element belongs to same group of A. The highest oxidation state oxides D and E of the elements which belong to the period of A react with solution B and give colourless solutions F and G respectively. When $BaCl_{2(aq)}$ is added separately to these solutions , white colour precipitates H and I are obtained respectively. When diluted HNO_3 is added to these precipitates, only H dissolves and gives a clear colourless solution.

i. Identify A,B,C,D,E,F,G,H and I.

A. **Na** B. **NaOH** C. **H_2**

D. **P_2O_5/P_4H_{10}** E. **SO_3** F. **Na_3PO_4**

G. **Na_2SO_4** H. **$Ba_3(PO_4)_2$** I. **$BaSO_4$**

ii. Write the balanced chemical equations for the chemical reactions described above.

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

$P_2O_5 + 6NaOH \rightarrow 2Na_3PO_4 + 3H_2O$

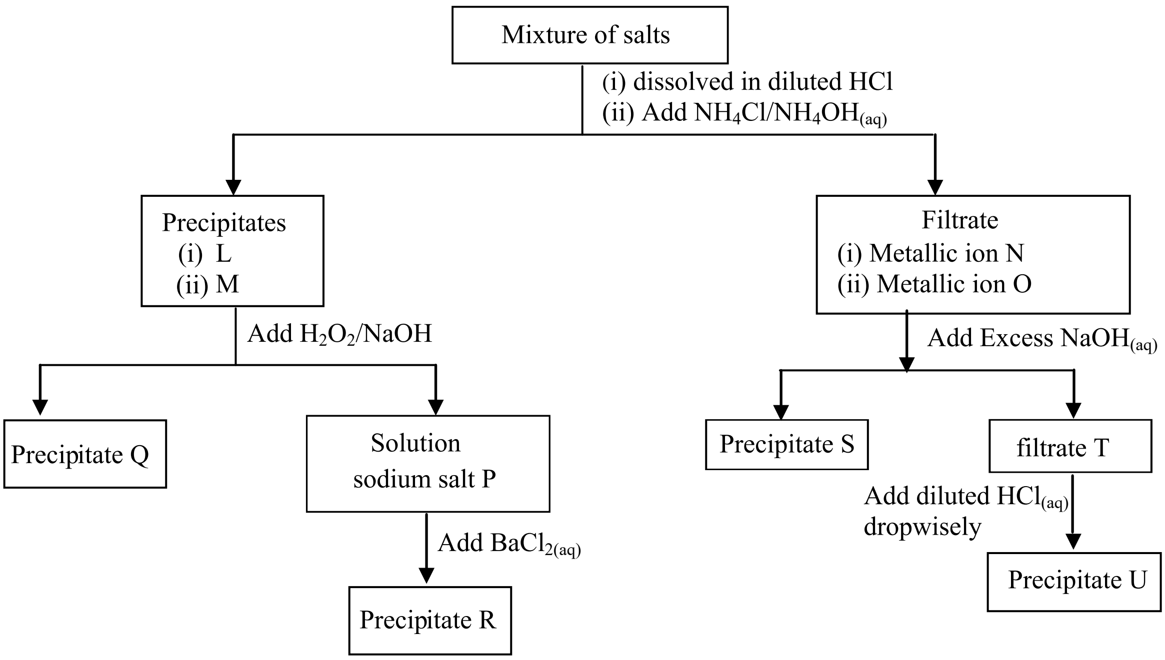
$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

$2Na_3(PO_4)_3 + 3BaCl_2 \rightarrow Ba_3(PO_4)_2 + 6NaCl$

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

$Ba_3(PO_4)_2 + 6HNO_3 \rightarrow 3Ba(NO_3)_2 + 2H_3PO_4$

(b) A flow chart for the analysis of a salts sample contanining $MgCl_2$,$Fe(NO_3)_3$,$Cr_2(SO_4)_3$ and $ZnCl_2$ is given below.



i. By considering the above flow chart, give the precipitates Q, R, S and U and the salts P and T which are present in the solution state.

P. **$Na_2CrO_{4(aq)}$** Q. **$Fe(OH)_{3(s)}$** R. **$BaCrO_{4(s)}$**

S. **$Mg(OH)_{2(s)}$** T. **$Na_2ZnO_{2(aq)}$** U. **$Zn(OH)_{2(s)}$**

[See page 6

ii. What is the colour of precipitate R? What will be the colour of resultant solution obtained when diluted HNO_3 is added to this precipitate R? Give the appropriate balanced chemical equation for this change.

Colour of the precipitate R……………… **Yellow** ………………

Colour of the resultant solution ……………… **Orange** ………………

Chemical equation ……………… **$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$** ………………

$2BaCrO_{4(s)} + 2HNO_{3(aq)} \rightarrow BaCr_2O_{7(aq)} + Ba(NO_3)_{2(aq)} + H_2O_{(aq)}$

iii. Give **a chemical test** with the relevant **observations** to identify the metal ions in the precipitates S and U.

Test :……… **Charcoal block test** ………………

Observations

S:……… **light red** ………………

U:……… **green** ………………

iv. Give a test to identify the cation present in the precipitate Q .

Dissolve the precipitate in $CH_3COOH_{(aq)}$

Add KSCN, blood red colour will be obtained.

Add $K_4[Fe(CN)_6]$, blue colour precipitate will be obtained. (Any other acceptable answers)

03. (a) At 25°C temperature, an aqueous solution S was prepared by adding two mono basic weak acids HA and HB each of initial concentration $1 moldm^{-3}$. The degree of dissociation of HA and HB in this solution were α and β and the dissociation constants of them were K_1 and K_2 respectively (At 25°C, $K_1 = 4x10^{-6} moldm^{-3}$ and $K_2 = 1.2 \times 10^{-5}$ $moldm^{-3}$).

i. Giving reasons, deduce which of the above two acids is more acidic.

……… **HB, reason; $K_2 > K_1$.** ………………

…………………………………

ii. Obtain a relationship, between the degree of dissociation α,β and dissociation constants K_1,K_2 of the above acids.

$$\underset{1-\alpha}{HA_{(aq)}} \overset{K_1}{\rightleftharpoons} \underset{\alpha}{H^+_{(aq)}} + \underset{\alpha}{A^-_{(Aq)}}$$ **Equilibrium concentration**

$$\underset{1-\beta}{HB_{(aq)}} \overset{K_2}{\rightleftharpoons} \underset{\beta}{H^+_{(aq)}} + \underset{\beta}{B^-_{(Aq)}}$$ **Equilibrium concentration**

By the law of equilibrium,

$$K_1 = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

$$K_1 = \frac{(\alpha+\beta).\alpha}{(1-\alpha)}$$

$$K_2 = \frac{[H^+_{(aq)}][B^-_{(aq)}]}{[HB_{(aq)}]}$$

$$K_2 = \frac{(\alpha+\beta).\beta}{(1-\beta)}$$

Ionizing amount of weak acids can be neglected

∴ (1- α) ≃ 1, (1- β) ≃ 1

$K_1 = (\alpha + \beta)\alpha$

$K_2 = (\beta + \alpha)\beta$

$K_1 + K_2 = (\alpha + \beta)\alpha + (\alpha + \beta)\beta$

$K_1 + K_2 = (\alpha + \beta)^2$

$\alpha + \beta = \sqrt{K_1 + K_2}$

[See page 7

Do not write anything here.

iii. Show that the pH of the solution S can be given as, pH = - ½ log(K_1 +K_2).

$[H^+_{(aq)}] = \alpha + \beta = \sqrt{K_1 + K_2}$

$pH = - \log [H^+_{(aq)}]$

$= - \log (K_1 + K_2)^{1/2}$

$= - ½ \log [K_1 + K_2]$

iv. Show that $\alpha + \beta = 4x10^{-3}$.

$\alpha + \beta = \sqrt{K_1 + K_2}$

$\alpha + \beta = \sqrt{16 \times 10^{-6}}$

$= \sqrt{16 \times 10^{-6}}$

$= 4 \times 10^{-3}$

v. Calculate the values of degree of dissociation α and β using the relationships obtained in part (ii) and (iv).

$K_1 = (\alpha + \beta)\, \alpha \; K_2 = (\alpha + \beta)\, \beta$

$\frac{\alpha}{\beta} = \frac{K_1}{K_2}$

$\frac{\alpha}{\beta} = \frac{4 \times 10^{-6}}{12 \times 10^{-6}}$

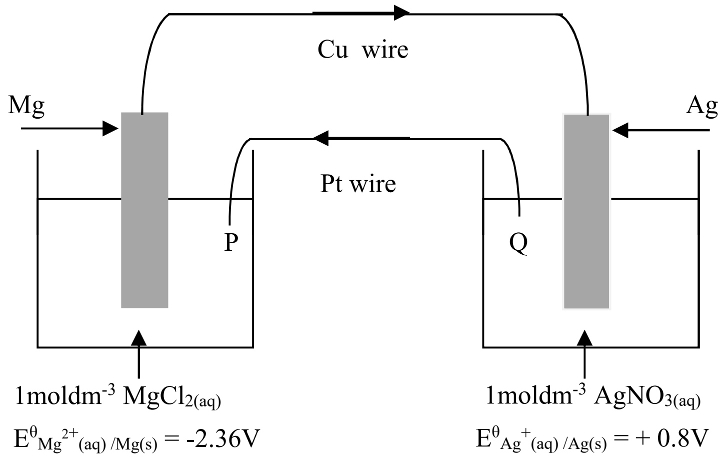
$\beta = 3\alpha$

$\alpha + \beta = 4 \times 10^{-3}$

$\alpha + 3\alpha = 4 \times 10^{-3}$

$\alpha = 1 \times 10^{-3}$, $\beta = 3 \times 10^{-3}$

(b) The following diagram shows a set up constructed by a student using standard Magnesium electrode, standard silver electrode, Pt wire and Cu wire.



i. Identify,whether the ends of Pt wires P and Q, Mg electrode and Ag electrode are positive terminal or negative terminal.

Mg **negative terminal** Ag **positive terminal**

P **positive terminal** Q **negative terminal**

ii. Mark the direction of electron flow in the Cu wire and Pt wire in the above circuit by using arrow marks.

iii. Give the electrode reactions of Mg and Ag electrodes.

$Mg(s) - 2e \rightarrow Mg^{2+}_{(aq)}$

$Ag^+_{(aq)} + e \rightarrow Ag(s)$

[See page 8

iv. Calculate the electric potential difference between Mg and Ag electrodes at the initial state?

$E^{\theta}_{cell} = E^{\theta}_{Cathode} - E^{\theta}_{Anode}$

$= +0.8V - (-2.36V)$

$= 3.16V$

v. Give the balanced chemical equations for the reactions take place at the ends P and Q of Pt wire which presents in the solution of two half cells.

P $2H^+_{(aq)} + 2e \rightarrow H_{2(g)}$ Or $2H_2O_{(l)} + 2e \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Q $4OH^-_{(aq)} - 4e \rightarrow O_{2(g)} + 2H_2O_{(l)}$ Or $2H_2O(l) - 4e \rightarrow 4H^+_{(aq)} + O_{2(g)}$

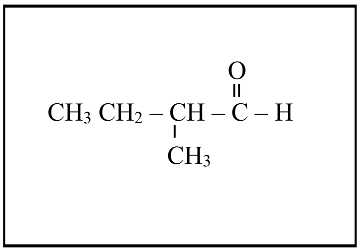
vi. Write the balanced chemical equations for the reactions take place at the terminals P and Q when Cu wire is used instead of Pt wire.

P $2H^+_{(aq)} + 2e \rightarrow H_{2(g)}$ Or $2H_2O_{(l)} + 2e \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

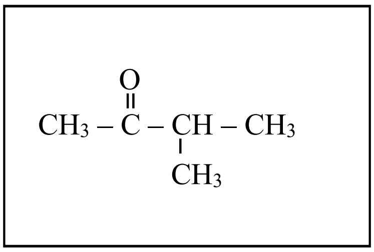
Q $Cu_{(s)} - 2e \rightarrow Cu^{2+}_{(aq)}$

04. (a) Organic compounds A, B, C, D and E have same molecular formula $C_5H_{10}O$. All these compounds can give orange colour precipitates with Brady's reagent. Only A exhibits optical activity. When the compounds A,B and C are reduced by $NaBH_4$ and involved to the dehydration, F,G and H are obtained as the products respectively. H exhibits diastereomerism. When H is treated with diluted H_2SO_4 and then oxidized by PCC, the compound D is obtained. When F and G are involved in hydration with diluted H_2SO_4, I is obtained as the only one product. "I" can give an instant turbidity with anhydrous $ZnCl_2$/con.HCl. The compound E does not involve to self condensation in diluted NaOH solution.

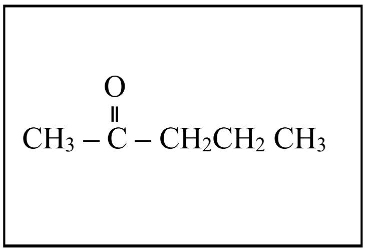
i. Give the structures of A, B, C, D, E, F, G, H and I in the boxes given below.



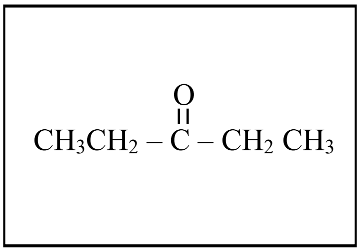
A



B



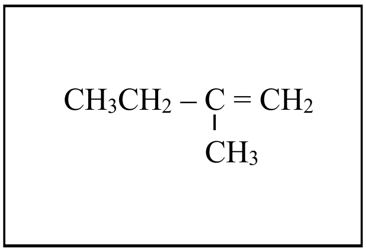
C



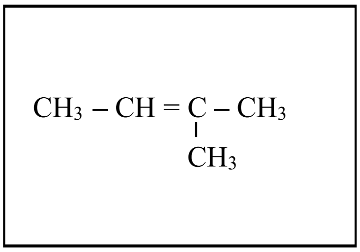
D

$(CH_3)_3 - C - CHO$

E



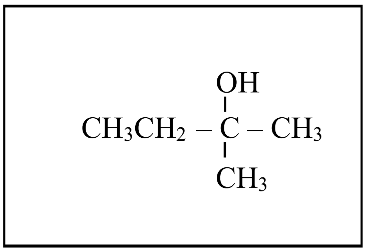
F



G

$CH_3CH_2 - CH = CH - CH_3$

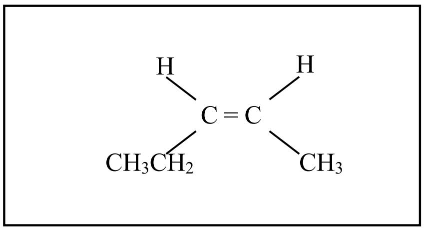
H

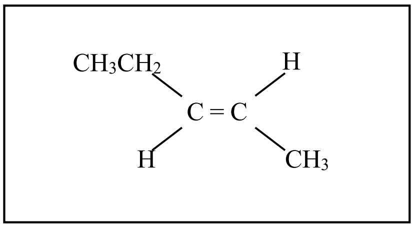


I

[See page 9

ii. Draw the structures of diastereomers of H.

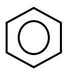
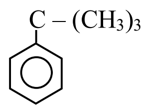
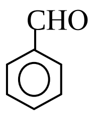
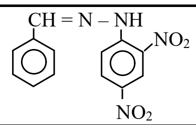
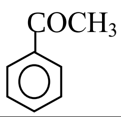
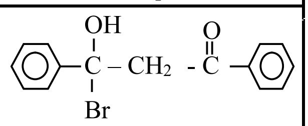




iii. Write the compounds F,G and H in the increasing order of their stability.

F < H < G

(b) The following table contains the reactants and reagents involved in the reactions from 1-6. Write down the type of reactions [nucleophilic addition (A_N), electrophilic addition (A_E), nucleophilic substitution(S_N), electrophilic substitution(S_E) and Elimination(E)] and the major products in the suitable cages.

	Reactant	Reagent	Type of reaction	Major Product
1	$CH_3CH{=}CH_2$	HBr	A_E	$CH_3-CH(Br)-CH_3$
2	$CH_3CH_2-C(Cl)-(CH_3)_2$	C_2H_5OH / KOH	E	$CH_3-CH=C-(CH_3)_2$
3	$CH_3C\equiv C-MgCl$	CH_3CH_2Cl	SN	$CH_3-C\equiv C-CH_2CH_3 + MgCl_2$
4		$CH_3-CH(CH_3)-CH_2Cl$ / Dry $AlCl_3$	SE	
5		2,4 - DNPH	AN + E	
6		dil $Ba(OH)_{2(aq)}$	AN	

(c) Write the mechanism for the following reaction.

$$(CH_3)_3-C-OH \xrightarrow{Con.HBr} (CH_3)_3-C-Br$$

$$(CH_3)_3-C-OH \xrightarrow{Con.HBr} (CH_3)_3-C-Br$$

$$(CH_3)_3-C-\ddot{O}H \;\; {}^{\delta+}H-Br^{\delta-} \longrightarrow (CH_3)_3-C-{}^{+}OH_2\ Br^-$$

$$(CH_3)_3-C-\overset{+}{O}H_2 \;\; :Br^- \longrightarrow (CH_3)_3-C-Br + H_2O$$

Essay part

05. (a) $NH_4Cl_{(s)} \rightleftharpoons NH_3(g) + HCl\ (g)$ $\quad Kp_1 = 3x10^8 Pa^2$

$\qquad\qquad P_1 \qquad P_1$

$NH_4Br(s) \rightleftharpoons NH_3(g) + HBr(g)$ $\quad kp_2 = 6\ x10^8 Pa^2$

$\qquad\qquad P_2 \qquad P_2$

(i) $Kp_1 = P_{NH3(g)} x\ P_{HCl(g)}$

$3\ x10^8\ Pa^2 = (P_1 + P_2)\ xP_1$ ……………….(1)

$Kp_2 = P_{NH3(g)}\ x\ P_{HBr(g)}$ ……………….(2)

$6x10^8 Pa^2 = (P_1 + P_2)\ x\ P_2$

(1) +(2) $9\ x10^8 Pa^2 = (P_1 + P_2)\ x\ P_1 + (P_1 + P_2)\ xP_2$

$(P_1 + P_2)^2 = 9x10^8 Pa^2$

$P_1 + P_2 = 3x\ 10^4 Pa$

$P_{NH3(g)} = 3\ x10^4 Pa$

(ii) $(1) \rightarrow P_1 = \dfrac{3 \times 10^8 Pa^2}{3 \times 10^4 Pa}$

$P_{HCl(g)} = 1\ x10^4 Pa$

$(2) \rightarrow P_2 = \dfrac{6 \times 10^8 Pa^2}{3 \times 10^4 Pa}$

$P_2 = 2\ x10^4 Pa$

$P_{HBr(g)} = 2\ x10^4 Pa$

(iii) In the new equilibrium, $P_{HCl(g)} = 6x10^3 Pa$, as the temperature does not change, Kp of the equilibrium $NH_4Cl(s) \rightleftharpoons NH_{3(g)} + HCl_{(g)}$ will not be changed.

$3\ x10^8 Pa^2 = P_{NH3(g)}\ x\ P_{HCl(g)}$

$3x10^8 Pa^2 = P_{NH3(g)}\ x\ 6\ x10^3 Pa$

$P_{NH3(g)} = 5\ x10^4 Pa$

In the new equilibrium, $P_{NH3(g)} = 5\ x10^4 Pa$

(iv) $Kp_2 = 6\ x10^8 Pa^2 = P_{NH3(g)}\ x\ P_{HBr(g)}$

$6\ x10^8 Pa^2 = 5\ x10^4 Pa\ x\ P_{HBr(g)}$

$P_{HBr(g)} = 1.2\ x10^4 Pa$

In the new equilibrium, $PHBr_{(g)} = 1.2\ x10^4 Pa$

In the new equilibrium,

$NH_4Cl(s) \rightleftharpoons NH_{3(g)} + \underset{x}{HCl_{(g)}}$

$NH_4Br(s) \rightleftharpoons NH_{3(g)} + \underset{y}{HBr_{(g)}}$

$P_{NH3(g)} = \ x + y$

$P_{NH3(g)} = P_{HCl(g)} + P_{HBr(g)}$

$5\ x10^4 Pa = 6\ x10^3 Pa + PHBr_{(g)}$

$P_{HBr(g)} = 44\ x10^3 Pa$

$2HBr_{(g)} \rightleftharpoons H_{(g)} + Br_{2(g)}$

Equilibrium pressure $44\ x10^3 - 2p \quad p \quad p$

$44\ x10^3 - 2p = 12\ x\ 10^3$

$P = 16\ x10^3$

$Kp = \dfrac{P_{H2(g)} \times P_{Br2(g)}}{P_{HBr(g)}}$ $\quad = \dfrac{16 \times 16}{12 \times 12}$

$= \dfrac{(16 \times 10^3 Pa)^2}{(12 \times 10^3 Pa)^2}$ $\quad = \dfrac{16}{9}$

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(b) i. WA (initial) = WA (EePH) + WA ($CHCl_3$)

17.5ppm x 100 x $10^{-3}dm^3$ = C_A x 100 x 10^{-3} dm^3 + 25ppm x 50 x 10^{-3} dm^3

C_A = 5 ppm

$$K_D = \frac{[A]_{CHCl3}}{[A]_{(l)}} = \frac{25\,ppm}{5\,ppm} = 5$$

ii. In experiment(i), initial $[A]_{(aq)} = \frac{1\times10^{-3}mol}{50\times10^{-3}dm^3} = 0.02moldm^{-3}$

$[B]_{(aq)} = \frac{2\times10^{-3}mol}{50\times10^{-3}dm^3} = 0.04moldm^{-3}$

In experiment(ii),

Initial $[A]_{(aq)}$x 50 x $10^{-3}dm^3$ + $[A]_{CHCl3}$ x 50 x$10^{-3}dm^3$ = 12 x10^{-3}mol

$S = \frac{[A]_{CHCl3}}{[A]_{(aq)}}$

$6[A]_{aq} = 0.24$ $\qquad [B]_{aq} = \frac{2\times10^{-3}mol}{50\times10^{-3}dm^3}$

$[A]_{aq} = 0.04moldm^{-3}$ $\qquad = 0.04moldm^{-3}$

In experiment(iii),

Initial $[A]_{(aq)}$ x 100 x $10^{-3}dm^3$ + $[A]_{CHCl3}$ x 100 x 10^{-3} dm^3=0.012mol

$S = \frac{[A]_{CHCl3}}{[A]_{(aq)}}$

$6[A]_{aq}$ =0.12

$[A]_{aq} = 0.02moldm^{-3}$

$$[B]_{aq} = \frac{0.002mol}{100\times10^{-3}dm^3} = 0.02moldm^{-3}$$

i. Rate = $k[A]^a[B]^b$

ii. 4 x$10^{-6}moldm^{-3}$ s^{-1} = k $(0.02moldm^{-3})^a$ $(0.04moldm^{-3})^b$ ………(1)

8 x$10^{-6}moldm^{-3}$ s^{-1} = k $(0.04moldm^{-3})^a$ $(0.04moldm^{-3})^b$ ………(2)

1 x $10^{-6}moldm^{-3}s^{-1}$ = k $(0.02moldm^{-3})^a$ $(0.02moldm^{-3})^b$ ....(3)

(2)/(1) a = 1

(1)/(3) b =2

iii. Over all order of the reaction = 1 + 2 = 3

iv. Rate =k $[A][B]^2$

4 x 10^{-6} $moldm^{-3}s^{-1}$ = k $(0.02moldm^{-3})$ $(0.04moldm^{-3})^2$

$$k = \frac{4\times10^{-6}}{32\times10^{-6}}mol^{-2}dm^6s^{-1}$$

$$k = 0.125mol^{-2}dm^6s^{-1}$$

(c) $nA = \frac{64g}{32gmol^{-1}} = 2mol$ $\qquad nB = \frac{46g}{46gmol^{-1}} = 1mol$

In the vapour state, $X_A = 0.75$

$X_A + X_B$ =1

$X_B = 0.25$

Using PV = nRT for the vapour system,

2.4 x10^5Pa x 8.314 x$10^{-3}m^3$ = n_{tot} x 8.314$Jmol^{-1}K^{-1}$ x 300K

n_{tot} = 0.8mol

n_A(Vapour) = 0.8mol x 0.75 = 0.6mol

n_B(vapour) = 0.2mol

In the solution, n_A = 2- 0.6 = 1.4mol $\qquad n_B$ = 1 – 0.2 = 0.8mol

In the liquid state, $X_A = \frac{1.4mol}{2.2mol} = \frac{7}{11}$ $\qquad X_B = 1 - X_A = \frac{4}{11}$

By Ravoult's law,

$P_A = P^0_A X_A = X_A^1 . P_T$

$$P_A = \frac{7}{11}P_A^0 = 0.75\times2.4\times10^5\,Pa$$

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$$P_A^0 = 0.75 \times 2.4 \times 10^5 \times \frac{11}{7} Pa$$
$= 2.82 \text{ x}10^5$Pa
$P_B = P^0_B . X_B = X_B{}^1 .P_T$
$$P_B^0 = 0.25 \times 2.4 \times 10^5 \times \frac{11}{4} Pa = 1.65 \times 10^5 \ Pa$$

06. (a) i. $B^+_{(aq)} + A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons BOH_{(aq)} + HA_{(aq)}$

$$K_b = \frac{[BOH_{(aq)}][HA_{aq)}]}{[B^+_{(aq)}][A^-_{(aq)}]}$$

$$K_a = \frac{[A^-_{(aq)}][H^+_{(aq)}]}{[HA_{(aq)}]} \Rightarrow \frac{[H^+_{(aq)}]}{ka} = \frac{[HA_{(aq)}]}{[A^-_{(aq)}]} \quad \text{…………..(2)}$$

$$K_b = \frac{[B^+_{(aq)}][OH^-_{(aq)}]}{[BOH_{(aq)}]} \Rightarrow \frac{[BOH_{(aq)}]}{[B^+_{(aq)}]} = \frac{[OH^-_{(aq)}]}{kb} \quad \text{………….(3)}$$

(1),(2),(3) $$Kh = \frac{[H^+_{(aq)}]}{ka} \times \frac{[OH^-_{(aq)}]}{kb}$$

$$Kh = \frac{kw}{ka \times kb}$$

ii.= From 1st equation, $Kh = \frac{[HA]^2}{[A^-]^2} = \frac{[H^+]^2}{ka^2} \left(\therefore [BOH] = [HA], [B^+] = [A^-]\right)$

$$\frac{kw}{ka.kb} = \frac{[H^+]^2}{ka^2}$$

$$[H^+]^2 = \frac{kw.ka}{kb}$$

$2\log[H^+] = \log kw + \log ka - \log kb$
$-2\log[H^+] = -\log kw - \log ka + \log kb$
$2pH = pkw + pka - pkb$
$pH = ½ (pkw + pka - pkb)$

iii. $pka = -\log ka = -\log 10^{-5} = 5$, $pkb = -\log kb = -\log 10^{-4} = 4$

$pkw = -\log kw = -\log 10^{-14} = 14$

(b) i.

	$NH_4OH_{(aq)}$ $\rightleftharpoons$	$NH_4^+{}_{(aq)}$ +	$OH^-_{(aq)}$	
Initial concentration / $moldm^{-3}$	0.1			α- degree of dissociation of NH_4OH
Reacted concentration/ $moldm^{-3}$	0.1α	0.1 α	0.1 α	
Equilibrium concentration/$moldm^{-3}$	0.1(1- α)	0.1 α	0.1 α	

$$kb = \frac{[NH^+_{4(aq)}]\left[OH^-_{(aq)}\right]}{\left[NH_4OH_{(aq)}\right]}$$

$$1 \times 10^{-5} moldm^{-3} = \frac{\left[OH^-_{(aq)}\right]^2}{0.1(1-\alpha)}$$

1- α Ω 1 என எடுக்க
$[OH^-_{(aq)}] = 1\text{x}10^{-3}\ moldm^{-3}$
$[H^+_{(aq)}][OH^-_{(aq)}] = 10^{-14} mol^2 dm^{-6}$
$[H^+_{(aq)}] = 10^{-11} moldm^{-3}$
$pH = -\log [H^+_{(aq)}] = -\log 10^{-11} = 11$

ii. $$n(NH_4)_2SO_4 = \frac{0.66g}{132\,gmol^{-1}} 0.005mol$$

$nNH_4^+ = 2n(NH_4)_2SO_4 = 2\text{x}0.005mol = 0.01mol$
$[NH_4^+{}_{(aq)}] = 0.01moldm^{-3}$
$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

	$NH_4OH_{(aq)}$	$NH_4^+{}_{(aq)}$	$OH^-_{(aq)}$	
Initial concentration / $moldm^{-3}$	0.1	0.01		
Reacted concentration/ $moldm^{-3}$	c	c	c	α-degree of dissociation of NH_4OH
Equilibrium concentration /$moldm^{-3}$	0.1- c	0.01+ c	c	

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$$kb = \frac{[NH^{+}_{4(aq)}][OH^{-}_{(aq)}]}{[NH_4OH_{(aq)}]}$$

when $[NH_4^{+}{}_{(aq)}]$ is high, ionization of NH_4OH is less

$0.1 - C \ \underline{\Omega}\ 0.1$ and $0.01 + C \ \underline{\Omega}\ 0.01$

$$1\times10^{-5}\,moldm^{-3} = \frac{0.01moldm^{-3}[OH^{-}_{(aq)}]}{0.1moldm^{-3}}$$

$[OH^{-}{}_{(aq)}] = 1x10^{-4}moldm^{-3}$

$[H^{+}{}_{(aq)}]\ [OH^{-}{}_{(aq)}] = 10^{-14}mol^{2}dm^{-6}$

$[H^{+}{}_{(aq)}] = 10^{-10}moldm^{-3}$

$pH = -\log [H^{+}{}_{(aq)}] = -\log 10^{-10} = 10$

When $M(OH)_2$ just starts to precipitate

$[M^{2+}{}_{(aq)}]\ [OH^{-}{}_{(aq)}]^{2} = ksp\ (M(OH)_{2(s)})$

$[M^{2+}{}_{(aq)}]\ (1x10^{-4}moldm^{-3})^{2} = 1x10^{-11}mol^{3}dm^{-9}$

$[M^{2+}{}_{(aq)}] = 10^{-3}moldm^{-3}$

$nM^{2+} = 10^{-3}moldm^{-3} \ x\ 1dm^{3} = 10^{-3}mol$

$nMCl_2 = nM^{2+} = 10^{-3}mol$

$WMCl_2 = 10^{-3}mol\ x\ 95gmol^{-1} = 0.095g$

iii. To just start the precipitation of $Ca(OH)_2$

$[Ca^{2+}{}_{(aq)}]\ [OH^{-}{}_{(aq)}]^{2} = ksp\ (Ca(OH)_{2(s)})$

$[Ca^{2+}{}_{(aq)}]\ (1x10^{-4}moldm^{-3})^{2} = 4\ x10^{-6}mol^{3}dm^{-9}$

$[Ca^{2+}{}_{(aq)}] = 400\ moldm^{-3}$

/ $nCa^{2+} = 400moldm^{-3}\ x\ 1dm^{3} = 400mol$

$nCaCl_2 = nCa^{2+} = 400mol$

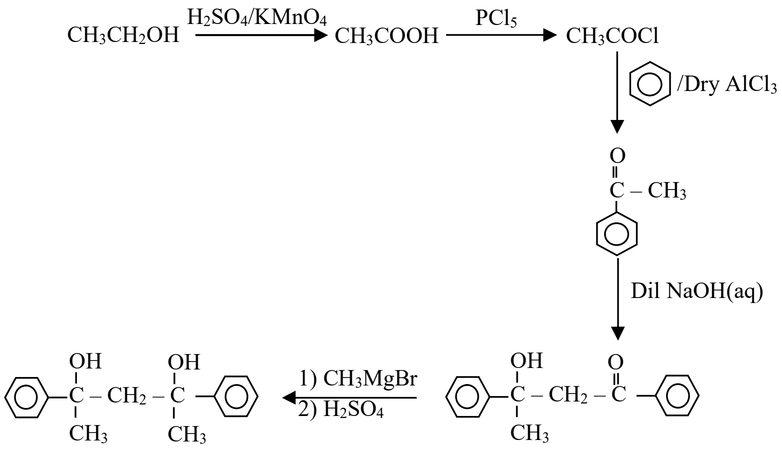
$WCaCl_2 = 400mol\ x\ 111gmol$

$= 44400g$

$= 44.4kg$

It is not suitable to dissolve 44.4kg of solid in $1dm^3$ of solution. Therefore $Ca(OH)_2$ can not be precipitated

07. (a)



$P_1 \rightarrow CH_2 = CH_2$

$P_2 \rightarrow CH_3 - CH_2 - Cl$

$P_3 \rightarrow CH_3CH_2NH_2$

$P_4 \rightarrow H - C \equiv C^-Na^+$

$P_5 \rightarrow CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$

$P_6 \rightarrow CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{O^-}{|}}{C}} - C \equiv CH$

$P_7 \rightarrow CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - C \equiv CH$

$P_8 \rightarrow CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - \overset{\overset{O}{\|}}{C} - CH_3$

$R_1 \rightarrow H_2/Pd/BaSO_4/$Quinoline

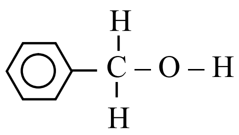
$R_2 \rightarrow HCl_{(g)}$

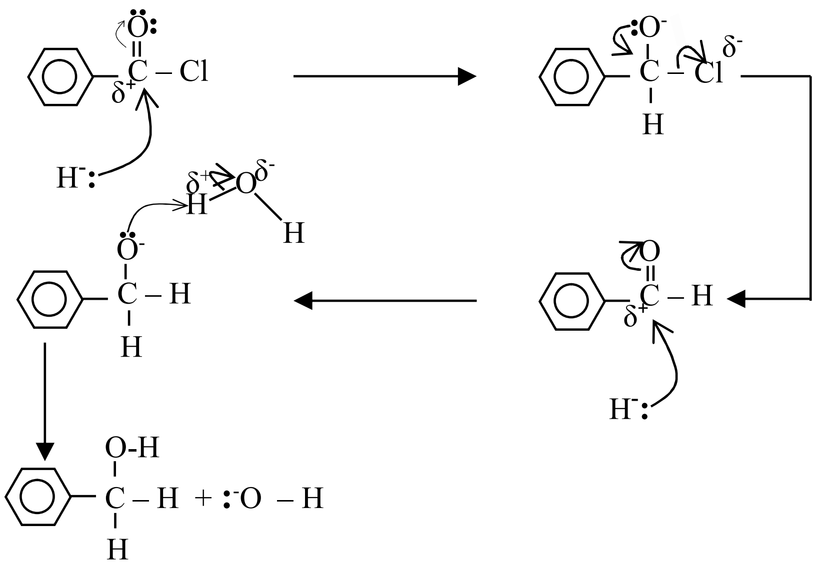
$R_3 \rightarrow$ C. $NH_{3(aq)}$

$R_4 \rightarrow Na$

$R_5 \rightarrow Hg^{2+}/$ dil H_2SO_4

$R_6 \rightarrow H_2O$





08. i. P- $BaCl_2$ Q – $BaSO_4$ R – CrO_2Cl_2
S - Na_2CrO_4 T – $BaCrO_4$ U – $BaCr_2O_7$

ii. Orange colour solution will turn yellow.
$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

(b) i. Al^{3+}, Mn^{2+}, Ca^{2+}

ii. P_3 – CaC_2O_4 P_4 – $Mn(OH)_2$ P_5 – $Al(OH)_3$

iii. 1. Add PbO_2, Con. H_2SO_4 violet colour solution will be obtained. Or
2. Melting by adding Na_2CO_3, KNO_3 green colour precipitate will be obtained

(c) i. $IO_3^-(aq) + 8I^-(aq) + 6H^+(aq) \rightarrow 3I_3^-(aq) + 3H_2O(l)$

ii. nIO_3^- used in step(I) $= 0.02 moldm^{-3} \text{ x } 25 \text{ x } 10^{-3} dm^3$.

$$= \frac{0.5}{1000} mol$$

But $nIO_3^- : nI_3^- = 1:3$

$$\therefore nI_3^- = \frac{3 \times 0.5 mol}{1000}$$

$$nI_3^- = \frac{1.5}{1000} mol$$

iii. $I_3^-(aq) + 2Na_2S_2O_3(aq) \rightarrow 3I^-(aq) + Na_2S_4O_6(aq) + 2Na^+$

$nNa_2S_2O_3(aq)$ used to react with remaining $I^{-3}_{(aq)}$ $= 0.1 moldm^{-3} \text{ x } 25 \text{ x } 10^{-3} dm^3$

$$= \frac{2.5}{1000} mole$$

But $nI_3^- : nNa_2S_2O_3 = 1:2$

Therefore reacted nI_3^- $= \frac{1}{2} \text{ x } \frac{2.5}{1000} mole$

$$= \frac{1.25}{1000} mole$$

Therefore, the amount of $nI_3^-(aq)$
Reacted with ascorbic acid $= \left(\frac{1.5}{1000} - \frac{1.25}{1000}\right) mole$

$$= \frac{0.25}{1000} mole$$

But ascorbic acid : $nI_3^-(aq) = 1:1$ The

amount of ascorbic acid in $25 cm^3$ $= \frac{0.25}{1000} mole$

$\therefore$ the amount of ascorbic acid in $500 cm^3 = \frac{0.25}{1000} \times 20 mole$

$$= \frac{5}{1000} \times mole$$

weight of ascorbic acid in $500 cm^3$ $= \frac{5}{1000} mole \times 176 gmol^{-1}$

$$= \frac{880}{1000} g$$

$$= 0.88 g$$

Mass of vitamin C tablet in $500 cm^3$ $= 2 \text{ x } 500 mg$
$= 1g$

The mass percentage of ascorbic acid in one vitamin C $= \frac{0.88g}{1g} \times 100$

$$= 88\%$$

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09. i. $R_1 - CaCO_3$ R_2 – sea water R_3 – Cork/C R_4 – air

ii. O_1 – heating O_2 - electrolysis O_3 – concentrating
O_4 – melting O_5 – fractional distillation

iii. $P_1 - CaO$ $P_2 - CO_2$ $P_3 - CaC_2$ $P_4 - C_2H_2$
$P_5 - Ca(OH)_2$ P_6 – mother solution $P_7 - NaCl$ $P_8 - CaSO_4$/ gypsum
$P_9 - Mg(OH)_2$ $P_{10} - MgO$ $P_{11} - NaOH$ $P_{12} - Cl_2$
$P_{13} - H_2$ $P_{14} - HCl$ $P_{15} - N_2$ P_{16} – other gases
P_{17}- NH_3 $P_{18} - C_2H_3Cl$ P_{19} – PVC $P_{20} - MgCl_2$
$P_{21} - Mg$ $P_{22} - NH_4Cl$ $P_{23} - NaHCO_3$

iv. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
NH_3 production through Haber process temperature $450^0C - 500^0C$
Pressure : 250atm catalyst Fe/Fe_2O_3 inducer Al_2O_3/K_2O
$Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + H_2O$

v. 1. Global warming
2. By absorbing and emitting IR rays, due to the change in dipole moment which is caused by the vibration bonds
3. CO_2
4. - Melting of ice in polar regions
- Increase in sea level
- Lower areas and islands getting drowned;
- Desertification occurs due to the removal of moisture in the soil
- Drop of pure water level
- Weather change occurs
- Change in biodiversity
5. As the amount of water vapour in the atmosphere remains constant, it doesn't contribute to the rise of temperature.
6. NO_2/NO
7. AR - $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
Or
$4NO_2 + O_2 + H_2O \rightarrow 4HNO_3$
By dissolving in water it reduces pH of rain water to a state, less than 5
GN – Absorbs and emits IR rays due to the change in dipole moment caused during the vibration.
OLD – By absorbing sun rays it forms free radicals and acts as catalyst.

$NO_2 \xrightarrow{hv} NO + O$

$NO + O_3 \longrightarrow NO_2 + O_2$

$O_2 \longrightarrow 2O$

$O + NO_2 \longrightarrow NO + O_2$

PCS – The radicals formed by the reaction with high energy rays, react with O_2 in lower atmosphere and produces O_3

8. SO_2 – by dissolving in water
$SO_2 + H_2O \rightarrow H_2SO_3$
$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$
$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$
SO_2 - By dissolving in water, after the oxidation by the atmospheric oxidants like O_2, O, OH
$SO_2 \xrightarrow{oxidizer} SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$
$H_2SO_4 \rightleftharpoons H^+ + HSO_4$

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9. Absorption using alkali substances like limestone ($CaCO_3$) and dolomite ($CaCO_3.MgCO_3$), CaO and MgO
$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$
$MgCO_3 + SO_2 \rightarrow MgSO_3 + CO_2$
$CaO + SO_2 \rightarrow CaSO_3$
$MgO + SO_2 \rightarrow MgSO_3$

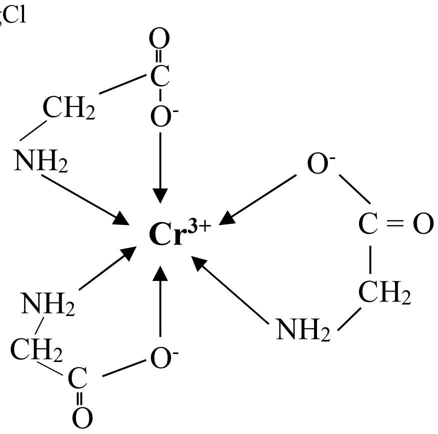
10. Cr_2O_3,CuO, Pt
$2NO_{(g)} + 2CO_{(g)} \rightarrow N_2(g) + 2CO_{2(g)}$
$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$

10. (a) i. +3 (+III)

ii. P – $[COBr(NH_3)_5]Cl_2$ Pentaamminebromidocobal(III) chloride
Q – $[CoCl\ (NH_3)_5\ BrCl$ – Pentaamminechioridocobalt (III) bromidechloride
R – $[COBr(NH_3)_5]$ BrCl –Pentaamminebromidocobalt(III) bromide chloride
S- $[COCl\ (NH_3)_5]Br_2$ Pentaamminechloridocobalt(III) bromide

iii. R- AgCl, AgBr
S – Only AgCl

iv.



(b) i. (1) $\Delta H^\theta = \sum H^\emptyset_{\text{Products}} - \sum H^\emptyset_{\text{Reactants}}$ = (2 x 0 + 2 x0) – (2x (-240kJmol^{-1}) + 2x0)
= 480kJmol^{-1}

(2) $\Delta S^\theta = \sum S^\emptyset_{\text{Products}} - \sum S^\emptyset_{\text{Reactants}}$
= (2 x 51Jmol^{-1}K^{-1} +0) – (2 x 59 Jmol^{-1}K^{-1} + 131Jmol^{-1}k^{-1}) = -147Jmol^{-1}K^{-1}

(3) $\Delta G^\theta = \Delta H^\theta - \Delta S^\theta$ = + 480kJmol^{-1} – 298K x (-147 x 10^{-3}) kJmol^{-1} = +523.806kJmol^{-1}

ii. (1) ΔH^θ = -480kJmol^{-1} (2) ΔS^θ = 147Jmol^{-1}K^{-1} (3) ΔG^θ = -523.806kJmol^{-1}

iii. From (ii) Since $\Delta G^\theta < 0$
The reaction $2H^+_{(aq)} + 2X(s) \rightarrow H_2(g) + 2X^+_{(aq)}$ will take place spontaneously at 25^0C and 1atm pressure.
Therefore, the reduction reaction, $2H^+_{(aq)} + 2e \rightarrow H_{2(g)}$ and oxidation reaction, $X_{(s)} \rightarrow X^+_{(aq)} + e$ are possible to occur. Hence the standard reduction potential of reaction $X^+_{(aq)} + e \rightarrow X_{(s)}$ will have a negative value. The standard electrode potential of H_2 is Zero. Electro chemical series is arranged according to the increasing order of reduction electrodes potentials. Therefore metal x lies above H_2 in the electrochemical series.

iv. (1) $X_{(s)} / X^+_{(aq)}$ ($H^+_{(aq)}/H_{2(g)}$/pt $_{(s)}$ or $H^+_{(aq)}$ / $H_{2(g)}$, $Pt_{(s)}$
(2) $X_{(s)} \rightarrow X^+_{(aq)}$ +e $2H^+_{(aq)} + 2e \rightarrow H_{2(g)}$
(3) $2H^+_{(aq)} + 2X_{(s)} \rightarrow H_{2(g)} + 2X^+_{(aq)}$
(4) $X_{(s)}/X^+_{(aq,1\ moldm\text{-}3)} \parallel H^+_{(aq,1\ moldm\text{-}3)} | H_{2(g,1atm)}/Pt_{(s)}$
(5) $\Delta G^\theta = -nFE^\theta$
$E^\theta = \Delta G^\theta$ /-nF = (-523.806kJmol^{-1})/(-2 x 96500 Cmol^{-1}) = 2.71V
(6) [X^+] should be decreased in the anodic region.[H^+] should be increased in the cathodic region. Pressure of $H_{2(g)}$ should be decreased. temperature of the cell should be decreased