Suggested solutions for SAJC 2008 Prelim Paper 3 (H2 Chemistry)

1(a)(i) $CrO_4^{3-} + 8H^+ + 2e \rightarrow Cr^{3+} + 4H_2O$

(ii) $2CrO_4^{3-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O + 2e$

(iii) $3CrO_4^{3-} + 10H^+ \rightarrow Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$

(b) No. of mole of $S_2O_3^{2-}$ = 0.30 x 32.00/1000 = 0.0096 mol

No. of mole of I_2 = ½ x 0.0096 = 0.0048 mol

Since $Cr_2O_7^{2-} \equiv 3I_2$

From equation (iii), $3CrO_4^{3-} \equiv Cr_2O_7^{2-}$

Thus, $Cr_2O_7^{2-} \equiv 3 I_2 \equiv 3CrO_4^{3-}$

No. of mole of CrO_4^{3-} = No. of mole of K_3CrO_4 = No. of mole of I_2 = 0.0048 mol

Mass of K_3CrO_4 used = 0.0048 x 233.3 = **1.12 g**

1(c) Mass = density x volume = $7.3 \times 0.5 \times 1.0 \times 10^{-5} \times 10^{6}$ = 36.5 g

No. of mole of Cr = $\frac{36.5}{52}$ = 0.702 mol

$Cr_2O_7^{2-}$ (or Cr^{+6}) + 6e $\rightarrow$ Cr(s)

6 F $\equiv$ 1 mole Cr

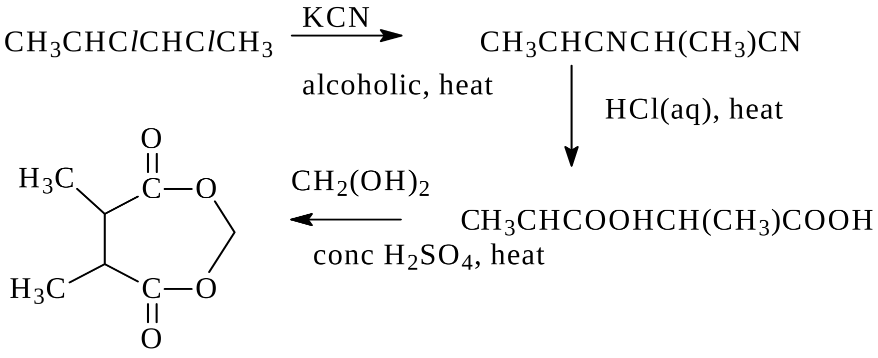
6 x 0.702 mol x 96500 C $\equiv$ 40 x time

Time = 10161.45 sec = **2.82 hr**

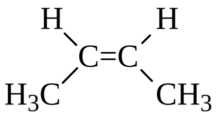
1(d) H_2O is preferentially reduced rather than Al^{3+} ions.

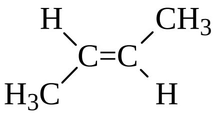
1(e) Cr^{3+}(aq) ion is coloured due to the splitting of the d-orbitals. The electronic repulsion between the water ligands and Cr^{3+} ion causes the degenerate 3d orbitals to undergo splitting, resulting in 2 groups of non-degenerate orbitals, with a small energy gap between them. By absorption of light energy, electrons can be promoted from a lower energy d-orbital to a higher energy d-orbital. This energy is related to the wavelength of the light absorbed, and the light not absorbed is thus seen as the colour of the complex**.**

1fi)

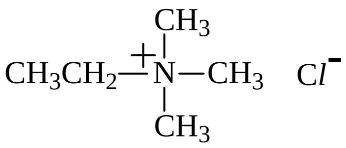


(ii) Geometric isomerism

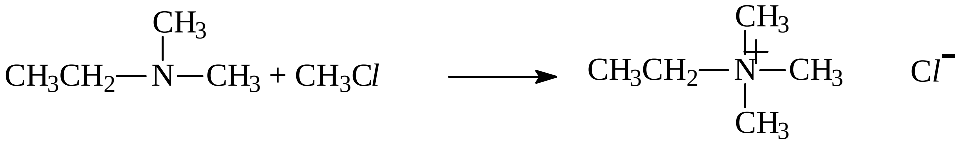




(iii)



$$CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{+}{N}}}-CH_3 \quad Cl^{-}$$



$$CH_3CH_2-\overset{\overset{CH_3}{|}}{N}-CH_3 + CH_3Cl \longrightarrow CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{+}{N}}}-CH_3 \quad Cl^{-}$$

2(a)(i) 2 assumptions for Ideal gas are :

- molecules in gaseous state do not exert any force or negligible forces of attraction;
- volume of molecules is negligibly small compared with that of the container.

ii) Set II because carbon dioxide will deviate most from ideal gas behaviour at low temperature and high pressure due to presence of attractive forces and significant molecular volume.

iii) Attractive forces operate among molecules at relatively short distances. At high pressure, density of gas increases, the molecules are much closer to one another and hence, gases condense into liquid.

2(b)(i) Let the solubility of $Ca(H_2PO_4)_2$ = s mol dm^{-3}

$$Ca(H_2PO_4)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,H_2PO_4^{-}(aq)$$

$$\begin{array}{ccc} s & s & 2s \end{array}$$

$K_{SP} = 1.0 \times 10^{-5} = (s) \times (2s)^2 = 4s^3$

$s = \sqrt[3]{[(1.0 \times 10^{-5})/4]} = 1.36 \times 10^{-2}$ mol dm^{-3}

No. of moles of $Ca(H_2PO_4)_2$ that can be dissolved in 100 cm^3 of water

$= 1.36 \times 10^{-2} \times 100/1000$ = **1.36×10^{-3} mol**

2(b)(ii) I. P. = $[Ca^{2+}]\,[H_2PO_4^{-}]^2$

$= [\,30/90 \times 3.0 \times 10^{-3}] \times [\,60/90 \times 3.0 \times 10^{-2}]^2$

$= (1 \times 10^{-3}) \times (2 \times 10^{-2})^2 = 4 \times 10^{-7}$ $mol^3\,dm^{-9}$

Since I. P. < K_{SP}, no ppt. occurs.

2(c)(i) BeO and Al_2O_3 are *amphoteric* as they show both acidic and basic properties.

$BeO(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + H_2O(l)$

$BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

OR:

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$

(ii) $Be(NO_3)_2(s) \rightarrow BeO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(iii) $Be(NO_3)_2$ > $Sr(NO_3)_2$

easier to decompose harder to decompose

Down the group, the cationic size increases and hence the charge density decreases. The polarizing power of the cations decreases down the group. Be^{2+} being smaller than Sr^{2+}, has the greater charge density and higher ability to polarise/distort the large electron cloud of the nitrate ion compared to Sr^{2+}. As a result, the N-O bond is weakened and the nitrate ion is more easily decomposed. Thus, $Be(NO_3)_2$ is easier to decompose than $Sr(NO_3)_2$.

2(d)(i) $MnO_2(s) + 4H^+(aq) + 2e \rightarrow Mn^{2+}(aq) + 2H_2O(l)$ +1.23 V

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e$ -0.77 V

$MnO_2(s) + 4H^+(aq) + 2Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + 2Fe^{3+}(aq)$ +0.46 V

Black solid pale green pale pink yellow

Since $E^0_{overall}$ = positive, the reaction is feasible.

(ii) $Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$ +1.36 V

$2Br^-(aq) \rightarrow Br_2(aq) + 2e$ - 1.07 V

$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$ +0.29 V

Yellow-green red-brown

Since $E^0_{overall}$ = positive, the reaction is feasible.

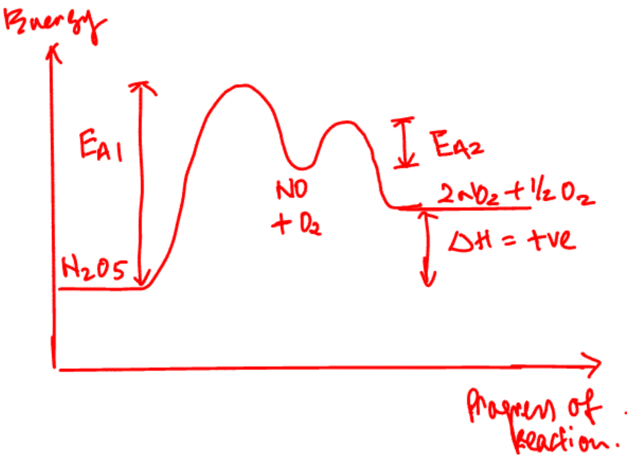
3ai) By measuring the changes in pressure/volume, or changes in colour with colorimeter.

ii) Graph of Time vs $[N_2O_5]$ gives constant half-life ➔ 1st order reaction w.r.t. N_2O_5.

Graph with at least two constant half-lifes, 22 min.

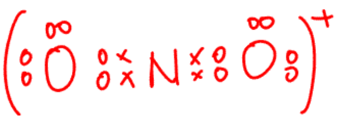
iii) $k = \ln 2/t_{1/2} = 0.693/22 =$ **$0.0315\ min^{-1}$**

3aiv)

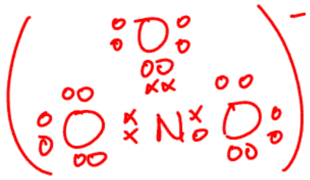


bii)

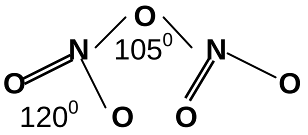
NO_2^+



NO_3^-



(ii)



3c

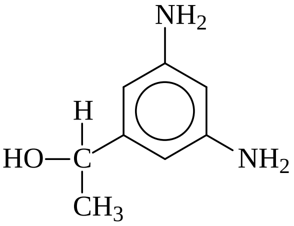
- ☑ Since D reacts with NaOH (aq) to form E & F, D contains either an <u>ester or an amide linkage</u>.
- ☑ Since $C_2H_4O_2$ gives effervescence with Na_2CO_3, $C_2H_4O_2$ contains –COOH group. $C_2H_4O_2$ is <u>CH_3COOH</u>.
- ☑ n F = 1.52/152 = 0.01 mol;

  n H_2SO_4 = 0.40 / 1000 x 25 = 0.01 mol

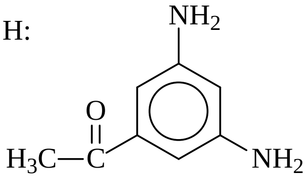
  Since n F / n H_2SO_4 = 1; hence F has <u>two amine groups</u>.
- ☑ Since F gives a white precipitate with Br_2, F must have a <u>phenylamine</u> group.
- ☑ Since F reacts with $K_2Cr_2O_7$, F contains a primary or secondary alcohol group.
- ☑ Since F reacts with alkaline aqueous iodine, F must contain the structure –$CH_3(OH)H$ and F must be secondary alcohol. (no marks given if students give -$CH_3C=O$ as F can be oxidised.)
- ☑ Since H reacts with alkaline aqueous iodine, H must contain the structure –$CH_3C=O$.

3c E: $CH_3COO^-Na^+$

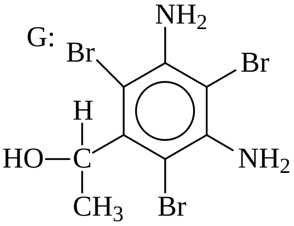
F:



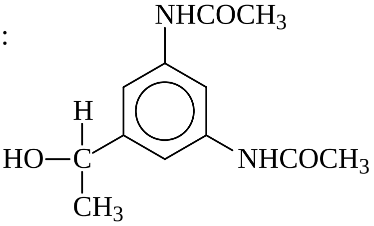
H:



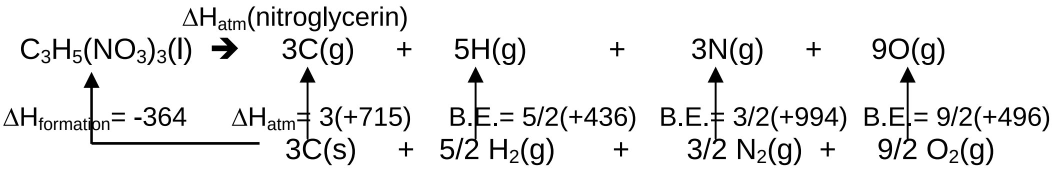
G:



D:



4ai)



ΔH_{atm}(nitroglycerin)

$C_3H_5(NO_3)_3(l) \rightarrow 3C(g) + 5H(g) + 3N(g) + 9O(g)$

$\Delta H_{formation}$= -364 ΔH_{atm}= 3(+715) B.E.= 5/2(+436) B.E.= 3/2(+994) B.E.= 9/2(+496)

$3C(s) + 5/2\ H_2(g) + 3/2\ N_2(g) + 9/2\ O_2(g)$

$\Delta H_{formation} + \Delta H_{atm} = 3(+715) + 5/2(+436) + 3/2(+994) + 9/2(+496)$

ΔH_{atm}(nitroglycerin) = +364 + 6958 = + 7322 kJ mol^{-1}

aii) $C_3H_5(NO_3)_3(l) \xrightarrow{\Delta H_{decomposition}} 3CO_2(g) + 5/2H_2O(g) + 3/2N_2(g) + 1/4O_2(g)$

aiii) $\Delta H_{decomposition} = \Sigma(\Delta H_{formation}$ Products$) - \Sigma(\Delta H_{formation}$ Reactants$)$

$= 3(-394) + 5/2(-242) - (-364)$

= **- 1423 kJ mol^{-1}**

aiv) $\Delta G^{\theta}_{decomposition} = \Delta H_{decomposition} - T\,\Delta S^{\theta}$

= - 1423 – [298 x (+208/1000)]

= **- 1485 kJ mol^{-1}**

Since ΔG^{θ} is negative, the reaction is spontaneous at 25^{0}C.

4av) The spontaneity is **not** affected by changes in temperature because $\Delta H_{decomposition}$ is negative, T is always positive and ΔS^{θ} is positive, i.e.

$\Delta G = \Delta H - T\Delta S$ = negative – [(+positive) x (+positive)] = negative

Thus, the decomposition reaction of nitroglycerin is spontaneous at all temperatures.

4(bi) In the presence of water, $AlCl_3$ undergoes hydrolysis to form an acidic solution.

$$[Al(H_2O)_6]^{3+}\text{ (aq)} + H_2O\text{ (}l\text{)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}\text{ (aq)} + H_3O^+\text{ (aq)}$$

The acidic nature of the solution is due to the relatively small but highly charged Al^{3+} ion which polarizes the surrounding water molecules to give up H^+ ions.

The acidic solution reacts with Na_2CO_3(s) to produce CO_2 gas.

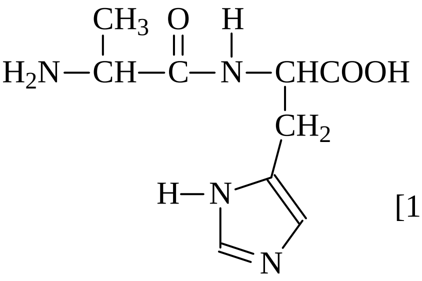
Whereas, Na*Cl* does not hydrolyse in water / Na*Cl* (aq) is neutral and therefore no CO_2(g) produced.

4bii) From Cr to Cu, electrons are added to **inner 3d orbitals.**

The 3d electrons **effectively shield** the outer 4s electrons from the increasing nuclear charge, nullifying the effect of the increasing nuclear charge across the period.

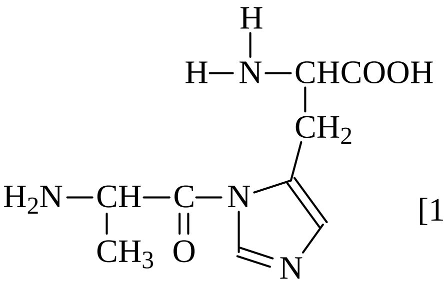
Thus, effective nuclear charge is almost constant and atomic radii remain almost constant from Cr to Cu as the increase in nuclear charge is minimal or insignificant.

4ci)



[1]

4cii)



[1]

4d) Ala-His-His-Pro-Ser

4ei) Hydrogen Bonding

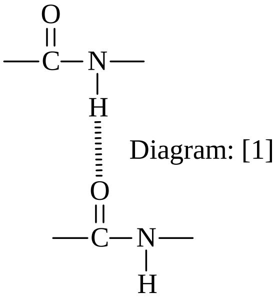


Diagram: [1]

4eii) At pH above and below 2, pepsin has denatured as the side chain groups with opposite charges / the ionic interaction between the side chain residues of the amino acids are broken which disrupts the tertiary structure / causes unfolding of the polypeptide chain.

5ai) on the addition of acid: $HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$

on the addition of alkali: $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

aii) $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ **OR:** $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$

$pH = pK_{a1} + \lg [HPO_4^{2-}]/ [H_2PO_4^-]$

$7.4 = 7.2 + \lg [HPO_4^{2-}]/ [H_2PO_4^-]$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \mathbf{1.58}$$

aiii) $[HPO_4^{2-}] + [H_2PO_4^-] = 2.0 \times 10^{-2}$ ------eq.(1)

$[HPO_4^{2-}] = 1.58\, [H_2PO_4^-]$

Substituting into eq.(1):

$1.58\, [H_2PO_4^-] + [H_2PO_4^-] = 2.0 \times 10^{-2}$

$[H_2PO_4^-] = \mathbf{7.75 \times 10^{-3}\ mol\ dm^{-3}}$

$\therefore [HPO_4^-] = 2 \times 10^{-2} - 7.75 \times 10^{-3} = \mathbf{1.23 \times 10^{-2}\ mol\ dm^{-3}}$

aiv) It is more difficult to remove H^+ ion from a more negatively charged ion, HPO_4^{2-}, than from a less negatively charged ion, $H_2PO_4^-$.

5b) B. pt. of HF > B. pt. of HBr > B. pt. of HC*l*

The boiling pt of HBr is higher than that of HCl because HBr has stronger Van der Waals forces of attraction due to its larger number of electrons than that of HCl. More energy is required to break the forces of attraction for HBr than HCl. HF has the highest boiling pt. due to the presence of intermolecular **hydrogen bonding** among the HF molecules. A larger amount of energy is required for the HF.

5c) $Mg^{2+} + 2e \rightleftharpoons Mg$ -2.38V

$Ca^{2+} + 2e \rightleftharpoons Ca$ -2.87V

$Na^+ + e \rightleftharpoons Na$ -2.71V

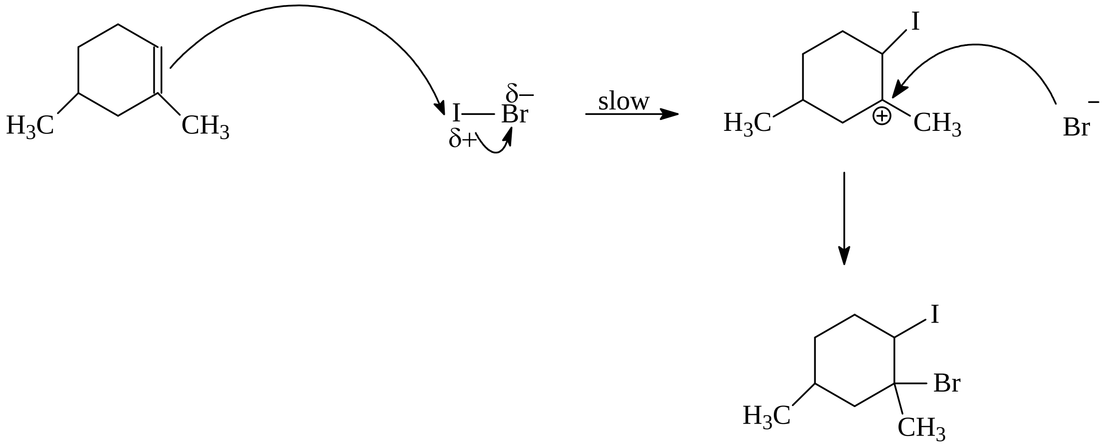
Mg^{2+} has the least negative $E^0_{reduction}$, hence it is most easily reduced / most easily dischaged at the cathode.

5di) Reagent: 2,4-dinitrophenylhydrazine

Condition: Heat or room temperature.

Observation: Carvone will form an orange ppt whilst 2,4 dimethylcyclohexene has no orange ppt is observed.

5dii)



5e) **Y** forms a white ppt AgCl **immediately** with $AgNO_3$ as Y has an electron deficient carbon on COCl as it is connected to oxygen which is electronegative making the carbon more susceptible to nucleophilic attack.

X forms a white ppt **after some time**

Z forms **no** ppt. as the lone pair of electrons on **Br and Cl** is delocalised into the pi electron system of the benzene ring. Hence the **C-Br and C-Cl** bond is strong and resistant to hydrolysis.