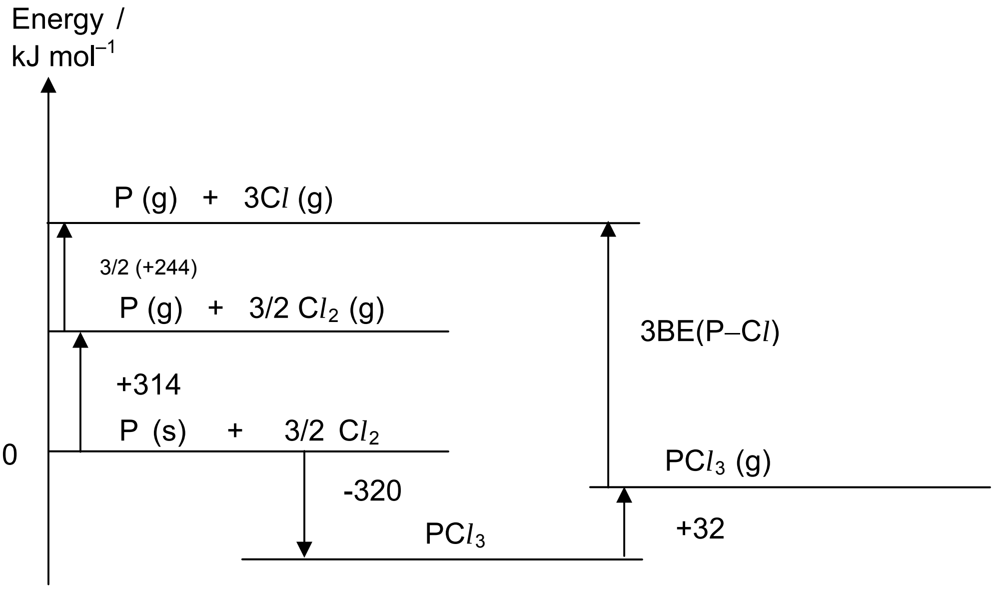
HWA CHONG INSTITUTION

2009 C2 Higher 2 CHEMISTRY 9746 PRELIMINARY EXAMINATION

PAPER 3 Free Response Questions (ANSWERS)

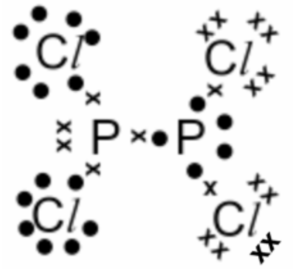
1 **(a)** **(i)**



-320 = 314 + 3/2(244) – 3BE(P–C*l*) -32

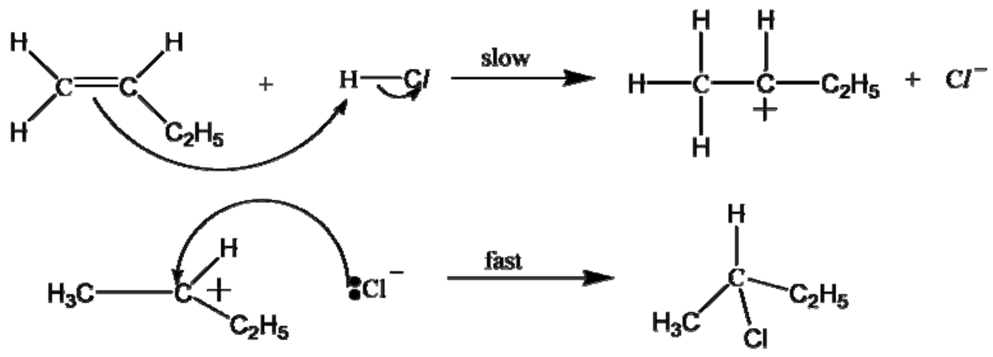
∴ BE(P–C*l*) = +323 kJ mol^{-1}

(ii)



Shape with respect to each P: Trigonal pyramidal; Bond angle: 107°

(b) **(i)** Electrophilic addition



(ii) Rate = k[but-1-ene][HCl]

(iii)

	BE / kJ mol^{-1}
H–Cl	431
H–I	299

The rate of reaction will be faster. The rate determining step involves the breaking of the H-X bond. Since H-I bond is weaker than H–Cl, the rate of reaction should be faster if HI is used.

(c) The product obtained will not rotate plane-polarised light, because the carbocation intermediate formed is planar.

Hence in the second step, there is an equal chance of the Cl^- ion attacking the carbocation from either side of the plane to produce equal amounts of the two enantiomers, giving rise to a racemic mixture.

The two enantiomers rotate plane-polarized light by equal amount and in opposite directions, hence cancelling each other's optical activity.

(d) **(i)** Both Cl_2 and I_2 exist as diatomic molecules and have dispersion forces existing between molecules.

I, being lower down in the group than Cl, has a bigger electron cloud size and hence, stronger dispersion forces. Therefore I_2 is less volatile than Cl_2.

(ii) $4Cl_2\,(aq) + S_2O_3^{2-}\,(aq) + 5H_2O\,(l) \rightarrow 8Cl^-\,(aq) + 2SO_4^{2-}\,(aq) + 10H^+\,(aq)$

$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$

	$E^{\ominus}$ / V
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1.36
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54

$E^{\ominus}_{Cl2/Cl-}$ is more positive than $E^{\ominus}_{I2/I-}$, indicating that Cl_2 is a stronger oxidizing agent than I_2. Hence, Cl_2 can oxidize $S_2O_3^{2-}$ to SO_4^{2-} while I_2 can only oxidize $S_2O_3^{2-}$ to $S_4O_6^{2-}$.

2 **(a)** **(i)** When a reversible reaction reaches a state of dynamic equilibrium, reaction continues to occur but the rates of the forward and backward reactions are equal such that there is no net change in the concentrations of the reactants and products.

(ii)

$$K_C = \frac{\left[Cr_2O_7^{2-}\right]}{\left[CrO_4^{2-}\right]^2\left[H^+\right]^2}$$

initial $[CrO_4^{2-}]$ = $\frac{8}{194.2} \div \frac{100}{1000} = 0.4119$ mol dm^{-3}

$[CrO_4^{2-}]$ at eqm = $\frac{1}{5}$ x $0.4119 = 0.08238$ mol dm^{Š3}

$[Cr_2O_7^{2-}]$ at eqm = $\frac{4}{5}$ x $0.4119 \div 2 = 0.1648$ mol dm^{Š3}

Substituting into K_C, $7.55 \text{ x } 10^{12} = \frac{0.1648}{(0.08238)^2\left[H^+\right]^2}$

$[H^+]$ = 1.793 x 10^{-6} mol dm^{-3}

pH = -lg (1.793 x 10^{-6}) = 5.75

(iii) When chromate ions are precipitated, the chromate concentration will drop and the equilibrium will shift to the left. This increases the amount of H^+ present and lowers the pH value.

(b) **(i)** $2CrO_4^{2-} + 3SO_2 + 10H^+ \rightarrow 2Cr^{3+} + 3H_2SO_4 + 2H_2O$
$E^{'}_{cell}$ = + 1.16 V

The overall cell potential (E_{cell}) for the redox reaction between CrO_4^{2-} and SO_2 is a large positive value, meaning that the reaction will go in the forward direction, i.e. chromate will be reduced to Cr^{3+}.

(ii) This could be due to the absence of water or H^+ ions in the atmosphere and on the painting / the amount of SO_2 in the atmosphere is low. Hence slowing down the rate of the reaction.

(iii) The pigment turns from yellow to green.

(c) **(i)** No. of moles of $S_2O_3^{2-}$ used = (21.50/1000) x 0.20 = 4.30 x 10^{-3}

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$
Hence no. of moles of I_2 formed in 25.0 cm^3 = 4.30 x 10^{-3} x ½ = 2.15 x 10^{-3}

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
$\Rightarrow$ mole ratio of $Cr_2O_7^{2-} : I_2 = 1 : 3$

No. of moles of $Cr_2O_7^{2-}$ reacted in 25.0 cm^3 = $(2.15 \times 10^{-3}) / 3 = 7.167 \times 10^{-4}$

No. of moles of $Cr_2O_7^{2-}$ present in 100 cm^3
= $200 \times 7.167 \times 10^{-4} / 25.0 = 5.733 \times 10^{-3}$

$[Cr_2O_7^{2-}]$ in sample = $5.733 \times 10^{-3} / (100/1000) = 0.0573$ mol dm^{-3}

(ii) **B** undergoes condensation with 2,4-DNPH to give a hydrazone, indicating it is an aldehyde or ketone.

However, **B** undergoes further oxidation with dichromate to give **C**. Hence **B** is an aldehyde, and **A** has a primary alcohol group. **C** is therefore a carboxylic acid.

B and **C** undergo oxidative cleavage with $KMnO_4$ to give CH_3CO_2H. Loss of 2 carbon atoms. Hence **B** and **C** contains alkene group, i.e. $CH_3C=C$ group.

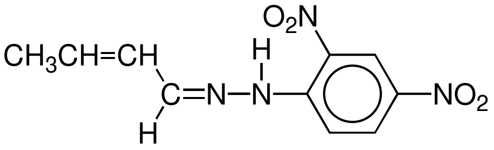
From the molecular formula of **A**,

A: $CH_3CH=CHCH_2OH$

B: $CH_3CH=CHCHO$

C: $CH_3CH=CHCO_2H$

Hydrazone:

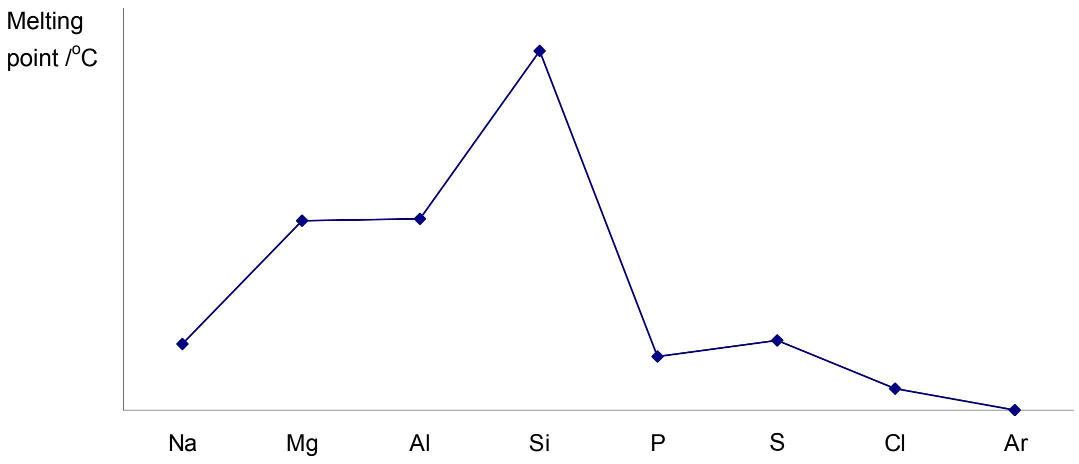


B undergoes reduction of alkene group and aldehyde group with hydrogen, while **C** undergoes reduction (or hydrogenation) of the alkene group only.

D: $CH_3CH_2CH_2CH_2OH$

E: $CH_3CH_2CH_2CO_2H$

3 **(a)**



High melting point from Na to A*l* as they exist as giant metallic structures with strong metallic bonds of increasing strengths due to smaller cationic radius and increased number of delocalized electrons.

Very high melting point for Si as it exists as a giant covalent structure with an extensive network of strong covalent bonds.

These strong bonds require a lot of energy to break before melting can occur.

Low melting point from P to Ar as they exist as simple molecular structures, consisting of discrete molecules with weak dispersions forces between the molecules.

Melting point decreases from $S_8 > P_4 > \mathrm{C}l_2 >$ Ar because the size of the electron clouds decreases from $S_8 > P_4 > \mathrm{C}l_2 >$ Ar, such that dispersion forces are weaker.

(b) $Mg(OH)_2$ is basic, and reacts only with acids:
$\mathrm{Mg(OH)_2(s) + 2HC}l\mathrm{(aq)} \rightarrow \mathrm{MgC}l_2\mathrm{(aq) + 2H_2O(}l\mathrm{)}$

$Be(OH)_2$ is amphoteric, and reacts with both acids and bases:
$\mathrm{Be(OH)_2(s) + 2HC}l\mathrm{(aq)} \rightarrow \mathrm{BeC}l_2\mathrm{(aq) + 2H_2O(}l\mathrm{)}$
$\mathrm{Be(OH)_2(s) + 2NaOH(aq)} \rightarrow \mathrm{Na_2Be(OH)_4(aq)}$

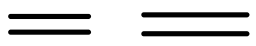
(c) **(i)** $\Delta G'_{\mathrm{soln}}$ for $MgSO_4$ = $(-91.2) - 298(-0.210) = -28.5$ kJ mol^{-1}
$\Delta G'_{\mathrm{soln}}$ for $BaSO_4$ = $(+26.3) - 298(-0.103) = +57.0$ kJ mol^{-1}

$MgSO_4$ is soluble but $BaSO_4$ is insoluble because $\Delta G'_{\mathrm{soln}}$ is negative only for $MgSO_4$.

(ii) The negative $\Delta S'_{\mathrm{soln}}$ indicates that there is a decrease in entropy when the two compounds dissolve to form aqueous ions. This could be due to a more orderly arrangement of H_2O molecules when the aqueous ions are formed.

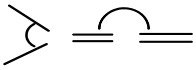
(d) **(i)** From pV = nRT, $32 \times 10^{3} \times 150 \times 10^{-6} = \dfrac{0.080}{M_r} \times 8.31 \times 303$

$M_r = 42.0$



{or CH_2CO}

(ii) Trigonal planar with respect to one C and linear with respect to the other C.



(iii) $CH_3CO_2C_2H_5$

(e) **(i)** **A** undergoes tri-iodomethane reaction ⇒ **A** contains $CH_3CH(OH)$- or CH_3CO- group.

From the given molecular formula, **A** is $CH_3CH(OH)CH_2CO_2H$.

A undergoes halogenation (nucleophilic substitution) with PCl_5 to form **B**. A contains –OH and/or $–CO_2H$ groups.

B is $CH_3CHClCH_2COCl$.

The –COC*l* group in **B** undergoes hydrolysis with water to give **C**.

C is $CH_3CHClCH_2CO_2H$.

C undergoes nucleophilic substitution with KCN, followed by acid hydrolysis to **D**.

D is $CH_3CH(CO_2H)\ CH_2CO_2H$.

C undergoes nucleophilic substitution with NH_3 to form **E**.

E is $CH_3CH(NH_3^+)\ CH_2CO_2^-$ (reject the molecular form)

4 **(a)** Any **two** properties:

Fe has a higher melting/boiling point than A*l*.
Fe has stronger metallic bonds as both the 3d and 4s electrons can be used in metallic bonding due to their proximity in energies, hence more energy is required to overcome the stronger bonds.

Fe has a greater density than A*l*.
Fe has a greater atomic mass but its atomic radius is smaller. Hence atomic volume is smaller. Since density = mass/volume, density of Fe is greater than A*l*.

Fe has better conductivity than A*l* as both the 3d and 4s electrons are available in the mobile sea of electrons due to the proximity in energy of 3d and 4s orbitals.

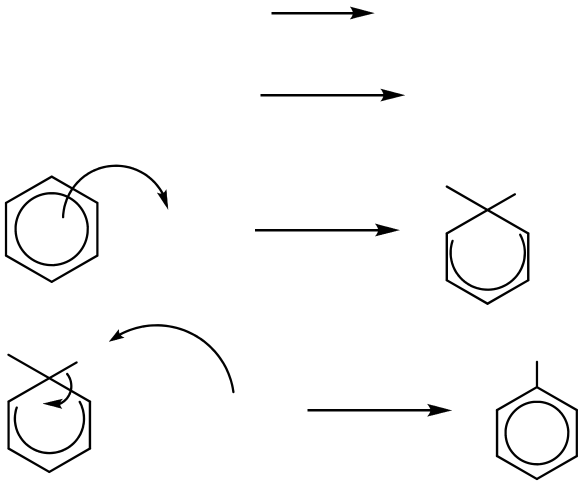
Fe is harder than A*l* due to stronger metallic bonding in Fe as Fe can use both its 3d and 4s electrons for metallic bonding due to the proximity in energy of 3d and 4s electrons.

(b) $_{26}\text{Fe}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ $_{13}\text{A}l$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
$_{26}\text{Fe}^{3+}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ $_{13}\text{A}l^{3+}$ $1s^2\ 2s^2\ 2p^6$

Although Fe has one more quantum shell than A*l* and higher nuclear charge, the increase in shielding effect due to the d electrons is proportionately less than the increase in nuclear charge, hence Fe experiences higher effective nuclear charge and is smaller.

Fe^{3+} has one more quantum shell than $\text{A}l^{3+}$ and the additional shielding is due to s and p electrons which are more effective in shielding compared to d electrons.

(c) **(i)** Electrophilic substitution



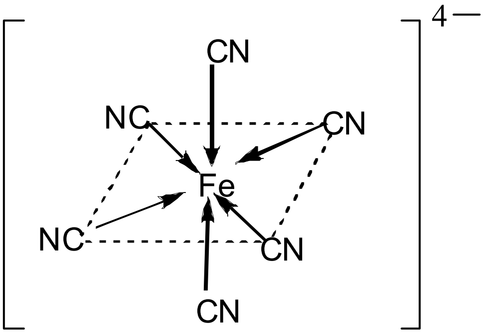
(ii) Phenol reacts with aqueous Br_2 at room temperature. No catalyst is required. The product formed is tri-substituted 2,4,6-tribromophenol, compared to monosubstituted product from benzene.

The -OH group in phenol activates the benzene ring towards electrophilic attack due to the delocalization of the lone pair electrons on O into the benzene ring.

(d) **(i)** **A** = $[Fe(H_2O)_6]^{2+}$
B = $[Fe(H_2O)_6]^{3+}$

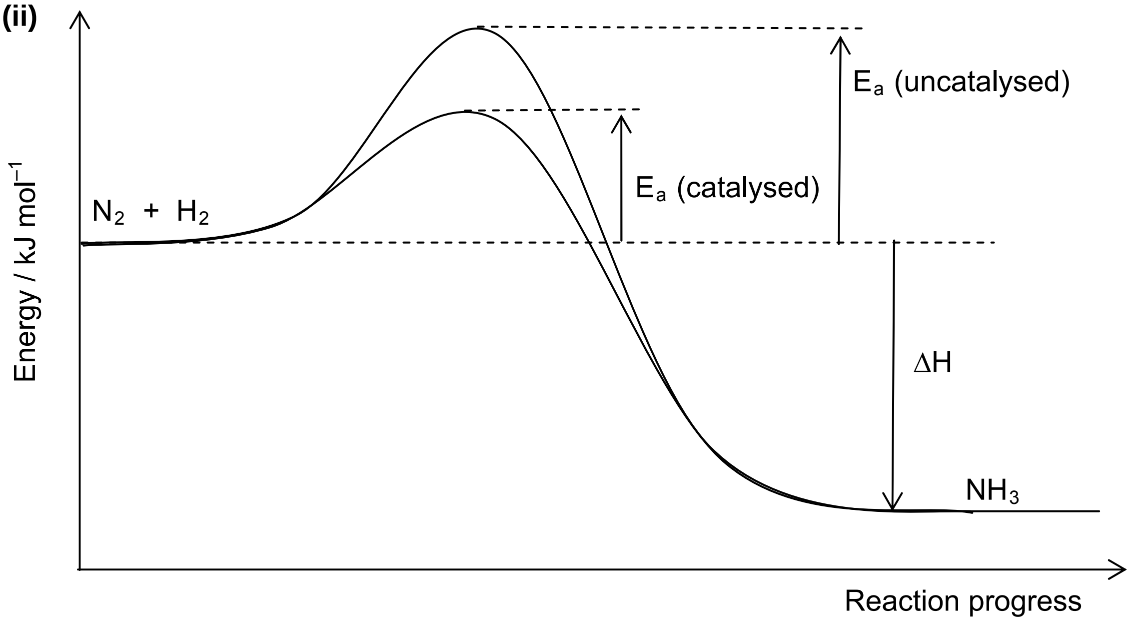
(ii) **X** = $K_2Cr_2O_7$ or $KMnO_4$ or Cl_2 or H_2O_2 (or in words)
Y = potassium thiocyanate or KSCN (or NH_4CN)

(iii)



(e) **(i)** This is due to the presence of partially-filled 3d subshells that can accept electrons from lone pairs or form temporary bonds with reactant molecules during adsorption, thus weakening the bonds in the reactant molecules and lowering the activation energy of the reaction.

(ii)



5 **(a)** **(i)** A solution that is able to resist pH changes when small quantities of acid or base are added.

(ii) When a small amount of OH^- is added, OH^- ions can be removed from the system by the reaction: $CO_2 + OH^- \rightarrow HCO_3^-$
{or $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$}
Hence pH remains almost constant.

(iii) $7.90 \times 10^{-7} = 10^{-7.4}\ [HCO_3^-]/[CO_2]$
$[HCO_3^-]/[CO_2]$ is 20:1

Blood has greater capacity for absorbing H^+ since there is a much higher concentration of the base component HCO_3^-.

(iv) CO_2 exhaled is recycled. Blood CO_2 level is raised and the buffer equilibrium shifts to the right thus increasing $[H^+]$. Hence blood pH will drop.

(b) **(i)** Quaternary structure refers to the arrangement of polypeptide chains (called sub-units) in a protein, which are held together by interactions between the side-chains of the polypeptides.

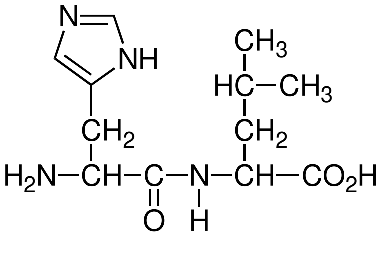
(ii) $$\text{Minimum } M_r = \frac{100}{0.34} \times 55.8 = 16\,412$$

There are four sub-units in each haemoglobin molecule.

(iii) Hydrophobic interactions

(c) **(i)** 1: dative bond; 2: hydrogen bond; 3: ionic linkage

(ii) Hydrolysis of the peptide linkage



{or zwitterion form}

(iii) Peptides are hydrolysed or broken down in gut or stomach by digestion.

(d) **(i)** Step 1: PCl_5; PCl_3 or $SOCl_2$
Step 2: NH_3 (g) (not aqueous)

(ii) Amide / diamide

(iii) Reduction

(iv)