ANDERSON SERANGOON JUNIOR COLLEGE

H2 Chemistry 9729 **2019 JC2 Prelim Exam Paper 3 Solutions**

1 (a) (i) $K_c = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$ [1]

units = $mol^{-1}\ dm^3$ [1]

(ii) $K_c = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

$4.99 \times 10^2 = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][5.00\times10^{-3}]}$

$\dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}]} = 2.495$ [1]

Let % of $Fe(SCN)^{2+}$ = x %, then % of Fe^{3+} = 100 – x,

$\dfrac{x}{100 - x} = 2.495$

$x = 249.5 - 2.495x$

$3.495x = 249.5$

$x = \dfrac{249.5}{3.495} = \underline{71.4\%}$ [1]

(iii) When temperature is increased (to 500 K), backward endothermic reaction is favoured, shifting the equilibrium position to the left to decrease the temperature by absorbing the extra heat. [1]

The red colour of the solution becomes less intense/fade. [1]

(b) Na, Mg and A*l* have giant metallic lattice structure with high melting points, as a large amount of energy is required to overcome the strong electrostatic forces of attraction between cations and sea of delocalised electrons. [1]

Melting point increases from Na to A*l* as the number of valence electrons for metallic bonding increases, and cationic radii decreases. Hence, metallic bond strength increases. [1]

Si has a giant molecular structure with high melting point as very large amount of energy is required to overcome the extensive covalent bonds between atoms in the three dimensional network structure. [1]
P_4, S_8 and Cl_2 have simple molecular structure with low melting points as small amount of energy is required to overcome the weak instantaneous dipole–induced dipole (id–id) attractions between the molecules. [1]

Melting point: $S_8 > P_4 > Cl_2$
- Number of electrons of $S_8 > P_4 > Cl_2$
- Hence, the strength of id–id attractions between the molecules decreases across the period from $S_8 > P_4 > Cl_2$

Amount of energy required to overcome the id–id attractions between the molecules decreases across the period from $S_8 > P_4 > Cl_2$ [1]

(c) (**B** and **C** could be metal oxides or chlorides due to the high melting points while **D** and **E** could be non–metal oxides or chlorides due to the low melting points.)

B is SiO_2 (as it has a high melting point, insoluble in water and only reacts with hot concentrated NaOH.)

Reaction of B with hot NaOH:
SiO_2 (s) + $2OH^-$ (aq) → SiO_3^{2-} (aq) + H_2O (l)

C is NaCl (as it has a high melting point and dissolves in water to form a neutral solution. Due to low charge density of Na^+, NaCl will not hydrolyse in water.)

D has a low melting point and dissolves in water to give an acidic solution. In addition, the ratio of **D** to precipitated Cl^- = 1: 5.

D is PCl_5
PCl_5 (s) + $4H_2O$(l) → H_3PO_4(aq) + 5HCl(aq)

E is SO_3
It has low melting point and dissolves readily in water to give a strongly acidic solution.
SO_3 (g) + H_2O (l) → H_2SO_4 (aq)

(It is an acidic oxide that reacts with aqueous sodium hydroxide in the ratio of 1:2.)
SO_3 (g) + $2OH^-$ (aq) → SO_4^{2-} (aq) + H_2O (l)

[6]

2 (a) (i) pV = nRT

$$n_1 = \frac{125 \times 101325 \times 60 \times 10^{-3}}{8.31 \times (273 + 27)}$$

= 304.8 [1]

$$\frac{125}{n_1} = \frac{50}{n_2}$$

$$\frac{n_1}{n_2} = 2.5$$

n_2 = 121.9 (number of moles of He remaining in the tank)

Number of moles of helium used to fill up the balloons
= 304.8 –121.9
= 183 mol [1]

(ii) At constant temperature $P_1V_1 = P_2V_2$. (Boyle's law)
$50 \times 60 \times 10^{-3} = 1.2 \times V_2$
V_2 = 2.5 m^3 [1]

Let n = number of balloons and V_b = the volume of each blown–up balloon.
$V_b = \frac{4\pi r^3}{3} = \frac{4\pi(0.15)^3}{3} = 1.414 \times 10^{-2}\ m^3$
$n = V_2/V_b = 176.8$

The remaining gas in the tank can fill up 176 balloons. [1]

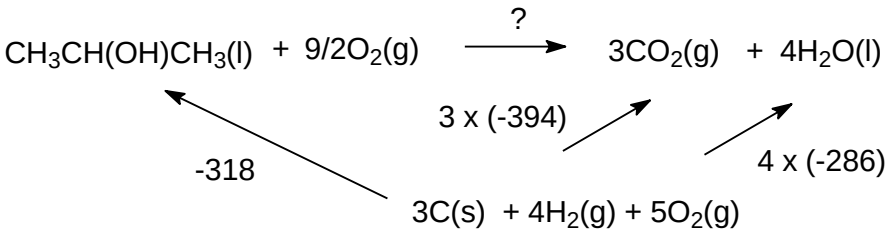
(iii) Helium behaves more ideally in balloons. [1]

Since the pressure is lower in the balloon (1.2 atm) as compared to in the tank (50 atm), the helium gas molecules will be further apart in the balloon.

The volume of the gas molecules therefore becomes insignificant compared to the volume of the balloon.

OR
The intermolecular forces of attraction are negligible. [1]

(b) **(i)**



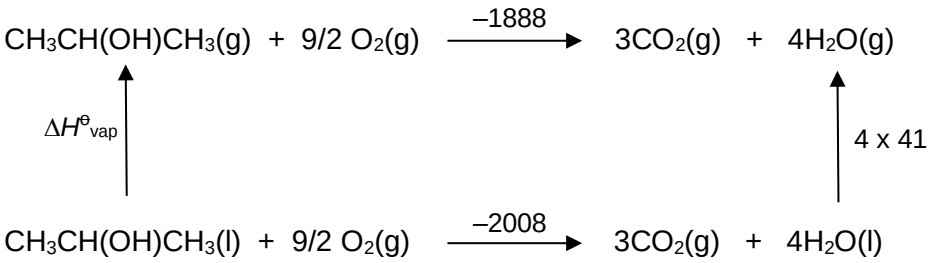
[1] for cycle

$\Delta H^{\ominus}_c$ = –(–318) + 3(–394) + 4(–286) = –2008 or –2010 kJ mol^{-1} [1]

(ii)

Energy taken in during Bond breaking	Energy released during Bond forming
2 x C–C = 2 x 350 7 x C–H = 7 x 410 1 x C–O = 1 x 360 1 x O–H = 1 x 460 9/2 x O=O = 4.5 x 496	3 x 2 x C=O = 6 x 805 4 x 2 x O–H = 8 x 460
6622	8510

$\Delta H^{\ominus}_c$ = 6622 – 8510 = –1888 kJ mol^{-1} [1]



$\Delta H^{\ominus}_{vap}$ = –2008 + 4 x (41) –(–1888) = +44.0 kJ mol^{-1} [1]

(iii)
- ΔH for combustion is negative
- ΔS for combustion is positive as the number of gaseous particles increases. [1]

- $-T\Delta S$ is negative
- Since $\Delta G = \Delta H - T\Delta S$
  ⇨ ΔG will always be negative and the reaction is spontaneous at all temperatures. [1]

(c) **(i)**

- (least acidic) 2–methylpropan–2–ol, 2,2–dimethylpropanoic acid, 2–chloro–2–methylpropanoic acid, (most acidic) [1]

Compare alcohol with acids:

- Both 2–chloro–2–methylpropanoic acid and 2,2–dimethylpropanoic acid are more acidic than 2–methylpropan–2–ol as the negative charge on the carboxylate ion is distributed equally [1] between the two O atoms and hence stabilises the ion to a greater extent. The dissociation of the acid to release H^+ is highly favoured.

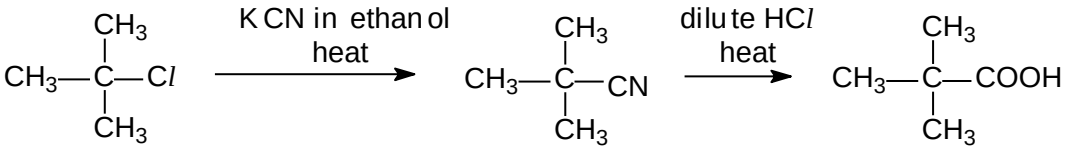
Compare 2,2–dimethylpropanoic acid with 2–chloro–2–methylpropanoic acid

- 2–chloro–2–methylpropanoic acid is the most acidic due to the presence of electron–withdrawing C*l* atom, which disperses the negative charge on the carboxylate ion to an even greater extent [1] and stabilises it more.

OR

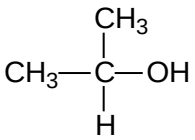
- 2,2–dimethylpropanoic acid is less acidic due to the presence of electron–donating alkyl (methyl) group, which intensifies the negative charge on the anion (carboxylate ion) and destabilises it. Therefore, the dissociation of this acid to release H^+ is less favourable.

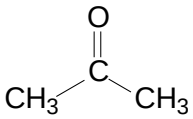
(ii)



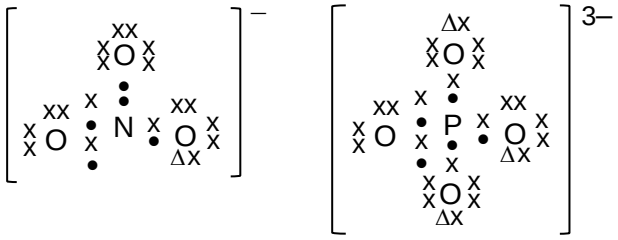
[1] [1] [1]

(iii) Step 1: aq. NaOH, heat [1]
Step 2: acidified $K_2Cr_2O_7$ or $KMnO_4$, heat [1]
Step 3: CH_3MgBr, followed by H_3O^+ [1]

G:  [1]

H:  [1]

3 **(a)** **(i)**



[1] each

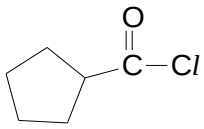
NO_3^-: trigonal planar
PO_4^{3-}: tetrahedral

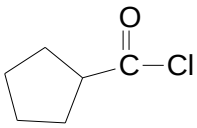
both correct shapes [1]

(ii) sp^2 [1]

(iii) The continuous overlap of p orbitals between the N and O atoms allow the lone pair / negative charge on the O atom to be delocalised into the N=O bond. [1]
As a result, all the N–O bonds have partial double bond character.
(or words to the same effect)

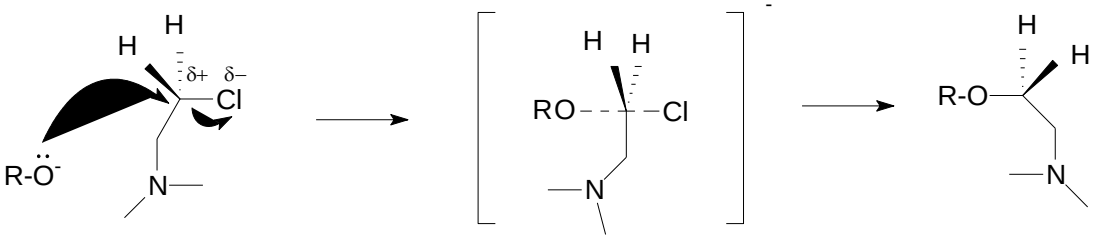
(b) **(i)** Step 1: CH_3COCl [1]
Step 2:

$AlCl_3$ and  [1]

(ii) 
If step 2 is carried out first, _____ can react with phenylamine via nucleophilic substitution, triggering an unwanted reaction. [1]

(iii) Sodium ethoxide is added as a base to deprotonate the phenol to generate a stronger nucleophile.

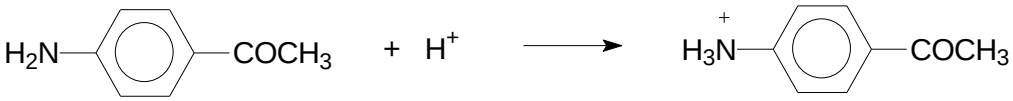
(iv) nucleophilic substitution (S_N2)



[3]

(v) Rate is ¼ times the original rate [1]

(vi) Phenol is more reactive towards electrophilic substitution. C=O attached to the benzene in K is electron–withdrawing [1] due to the more electronegative O atom. This will reduce the electron density of the benzene ring, making it less susceptible to be attacked by an electrophile/for electrophilic substitution [1].

(c) **(i)** 

4–aminoacetophenone undergoes acid–base reaction with HCl [1] to form an anion salt. Being ionic, it can form favourable ion–dipole interactions with water molecules [1], making it soluble in water.

Acetanilide has a neutral amide functional group and will not undergo acid–base reaction with HCl. Hence, it exists as molecular form which is insoluble in water due to non–polar benzene ring. [1]

(ii) 1. Dissolve the mixture in aqueous mineral acid such as dilute HCl or H_2SO_4.
2. Filter the mixture to recover the solid acetanilide.
3. Add excess aq NaOH to the filtrate (aqueous solution) until the solid reappears
4. Filter the mixture to recover the solid 4–aminoacetophenone.

[2]

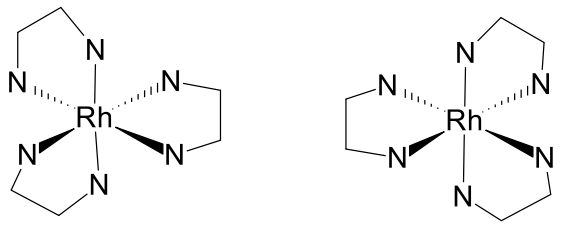
4 (a) (i) A ligand is a neutral molecule or an anion that has at least one lone pair of electrons to be used in forming a dative bond to the central metal atom or ion. [1]

(ii) +1 [1]

(iii) **M** is a catalyst since it is reacted/consumed in step 1 and regenerated in step 4 of the mechanism. [1]

N is an intermediate since it is formed in step 2 and reacted/consumed in step 3 of the mechanism. [1]

(v)



Either structure [1]

(b) (i) $[V(H_2O)_6]^{2+}$ has an oxidation number of +2, with 3 electrons in the 3d subshell. $[V(H_2O)_6]^{3+}$ has an oxidation number of +3, with 2 electrons in the 3d subshell.

The different electronic configurations OR different number of d electrons cause magnitude of the energy gap (ΔE) to be different. [1]

Since the ΔE is different in the different complex ions, the colours of the complex ions are different.

(ii) $NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O \quad E^\ominus = +0.96$ V
$V^{3+} + e \rightleftharpoons V^{2+} \quad E^\ominus = -0.26$ V

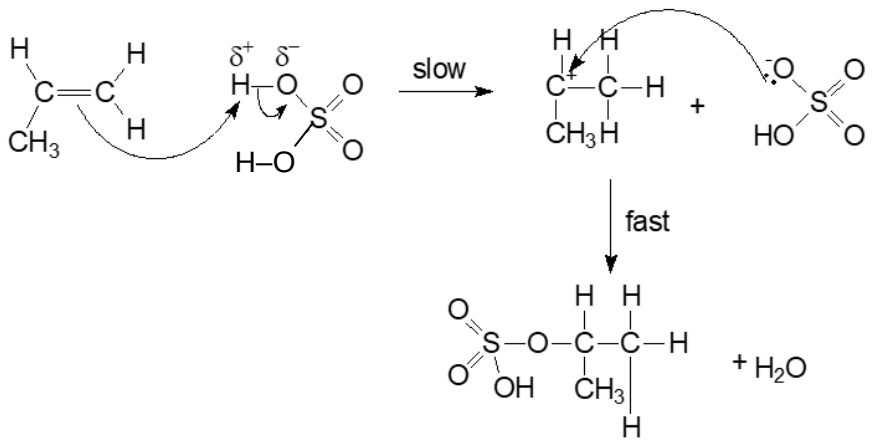
$E^\ominus_{cell} = +0.96 - (-0.26) = +1.22$ V > 0

$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O \quad E^\ominus = +0.96$ V
$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O \quad E^\ominus = +0.34$ V

$E^\ominus_{cell} = +0.96 - (+0.34) = +0.62$ V > 0
Products: VO^{2+}, NO and H_2O [1]

Overall equation: $3V^{2+} + 2NO_3^- + 2H^+ \longrightarrow 3VO^{2+} + H_2O + 2NO$ [1]

(c) (i)



[1] displayed formula of H_2SO_4
[2] mechanism

(ii) A more substituted (secondary) carbocation intermediate, which is more stable is produced in the first step. (since a 2° C^+ has more electron–donating alkyl groups bonded to the C^+ to disperse the positive charge). [1]

(d) **(i)** $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1]

(ii) $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad E^\ominus = +1.33$ V

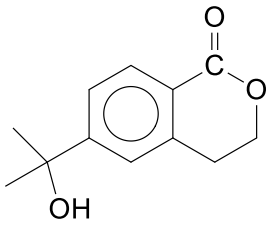
$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e \quad E^\ominus = +0.17$ V

$E^\ominus_{cell} = +1.33 - (+0.17) =$ +1.16 V [1]

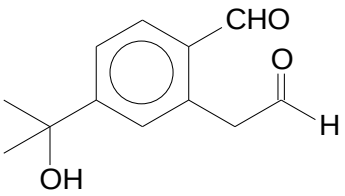
$\Delta G^\ominus = -nFE^\ominus_{cell}$
$= -6(96500)1.16$
$=$ 672 000 J mol^{-1} OR –672 kJ mol^{-1} [1]

(iii)

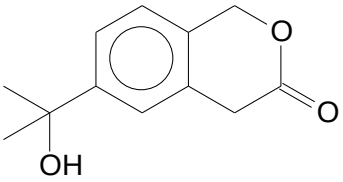
P:



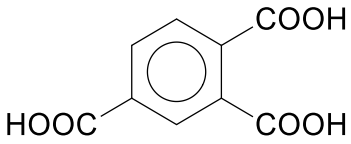
OR



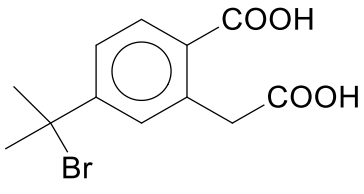
OR



Q:



S:



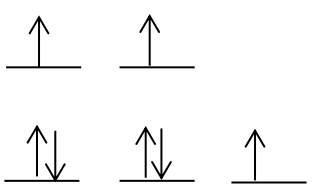
[1] each

(iv) C*l* 2 is more reactive than C*l* 1 [1]

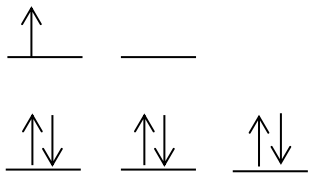
The C atom of the acyl group is highly electron–deficient, since it is bonded to two highly electronegative atoms, O and C*l*, while the C atom bonded to C*l* in alkyl chloride is only bonded to one electronegative atom, C*l*. [1]

OR nucleophile approaching the planar sp^2 carbon in acyl chloride experiences less steric hindrance than the tetrahedral sp^3 carbon in alkyl chloride.

5 (a) (i)



high spin state



low spin state

[1] each

(ii) The high spin state as it has a greater number of unpaired electrons. [1]

(iii)

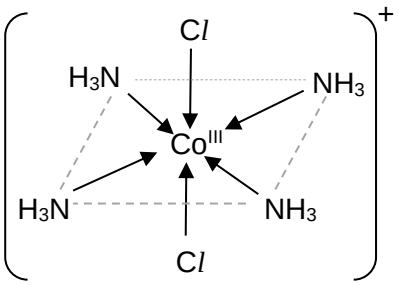
	Co	N	H	C*l*
% by mass	25.2	24.1	5.1	45.6
A_r	58.9	14.0	1.0	35.5
%/A_r	0.428	1.72	5.1	1.28
simplest ratio	1	4	12	3

Empirical formula: $CoN_4H_{12}Cl_3$ [1]

(iv) $n AgCl = \frac{1.43}{107.9 + 35.5} = 9.97 \times 10^{-3}$ mol ≈ 0.01 mol

no. of moles of Ω: AgC*l* = 1 : 1

Hence, the six ligands around the cobalt ion are 4 NH_3 and 2 Cl^- ligands.



or the 2 Cl^- ligands placed diagonally to each other at the equatorial positions [2]

(b) (i) Cathode: $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Overall: $2NiO(OH) + 2H_2O + Cd \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

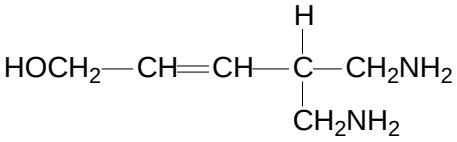
[1] for each equation (no need state symbols)

(ii) Mass of Cd to be restored = 100/86 x 5.5 = 6.395 g
n(Cd) = 6.395 / 112.4 = 0.0569 mol
n(electron) involved = 2 x 0.0569 = 0.1138 mol
Amount of charge required = 0.1138 x 96500 = 10982 C

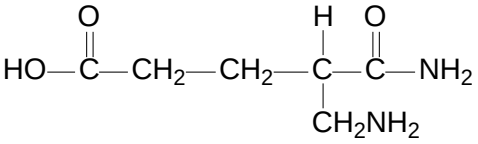
Q = I x t
⇒ 10982 = 2.0 x t
time = 5491 s = 1.53 h

[1]: n(electron) required
[1]: charge required
(scaling to 100% can be done at any point before calculating the time)
[1]: answer expressed in hours

(c)



I



J

[1] each

(d)

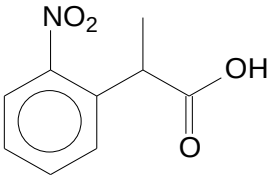
- W contains a <u>chiral carbon</u> since it rotates plane polarised light.
- W contains a <u>nitrobenzene</u> as it undergoes <u>reduction</u> with tin and concentrated HC*l* to form X which is a <u>phenylamine</u>.
- X contains a <u>–COOH group</u> since it undergoes <u>acid–base reaction</u> with sodium hydrogencarbonate to give carbon dioxide.
- X undergoes <u>electrophilic substitution</u> with Br_2(aq) to give compound Y, $C_9H_9NO_2Br_2$

  → Since only 2 Br are substituted, <u>one of the 2, 4, 6 positions relative to $–NH_2$ group on benzene has another substituent.</u>
- The –COOH in X undergoes <u>nucleophilic (acyl) substitution</u> with PCl_5 to give –COC*l*
- which then undergoes intramolecular <u>nucleophilic (acyl) substitution</u> to form Z.

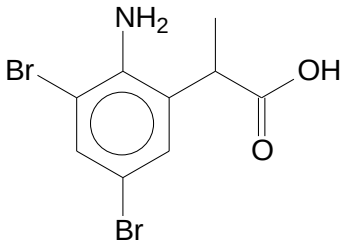
  ($–NH_2$ group in X attacks the electron deficient acyl C in the –COC*l* group)

  → <u>$–NH_2$ and –COOH groups on benzene ring are at positions 1 and 2 / next to each other</u>.

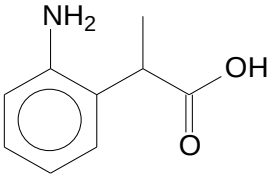
W:



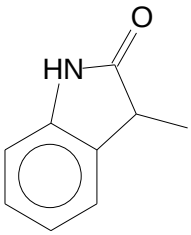
Y:



X:



Z:



[1] for each structure
[1] for every 2 correct deductions (max 3)