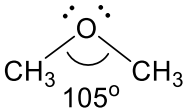
2020 RI H2 Chemistry Prelim Paper 3 – Suggested Solutions

Section A

1(a)(i)

OR

1(a)(ii)



CH_3OCH_3 has 2 bond pairs and 2 lone pairs around O, hence it has a bent shape. Since lone pairs exert a greater repulsion than bond pairs, it has a bond angle of 105°

1(a)(iii) The permanent dipole-permanent dipole (pd-pd) intermolecular forces in CH_3OCH_3 is stronger than the pd−pd intermolecular forces in CF_2CI_2. This is because CH_3OCH_3 has a greater net dipole moment than CF_2CI_2.

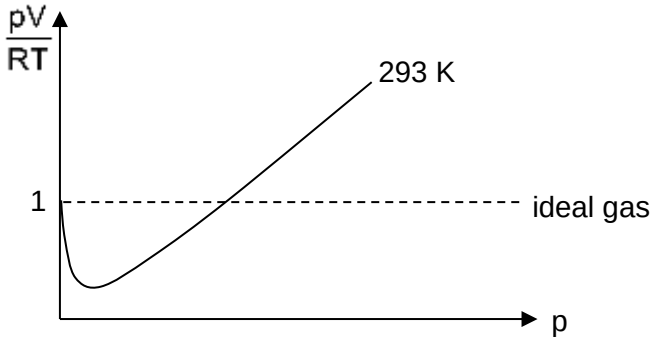
1(b)(i) The two assumptions are:

- The gas particles exert negligible attractive forces/intermolecular forces of attraction on each other.
- The volume of gas particles is negligible.

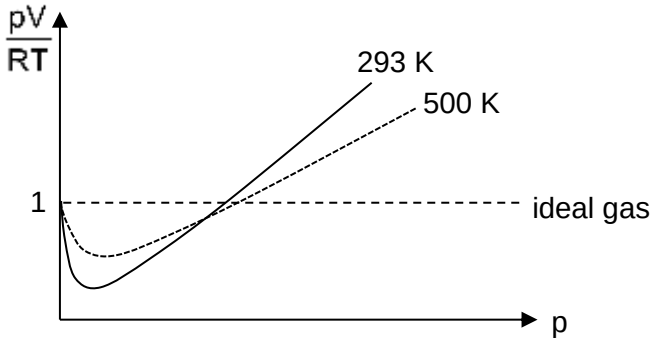
Other assumptions:

- The gas particles are in constant random motion.
- Collision between gas particles are perfectly elastic.
- The average kinetic energy of gas particles is proportional to absolute temperature.

1(b)(ii)



1(b)(iii)



At higher temperature of 500 K, the N_2O gas molecules have <u>higher kinetic energy</u> and are able to overcome the intermolecular attractive forces. Therefore, the <u>intermolecular attractive forces between them are less significant</u> and the N_2O gas molecules deviate from ideality to a smaller extent.

1(c)(i) $K_p = \dfrac{P_{CH_3OCH_3}P_{CO_2}}{(P_{CO})^3\,(P_{H_2})^3}$ units: atm^{-4} OR Pa^{-4}

1(c)(ii) $pV = nRT$

$p = nRT/V$

Partial pressure of CH_3OCH_3 at equilibrium $= \dfrac{732 \times 8.31 \times 500}{101325 \times 10}$

$= 3$ atm (shown)

1(c)(iii) Let the initial partial pressure of CO be x.

	$3CO(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$CH_3OCH_3(g)$	$CO_2(g)$
initial / atm	x	40 – x		0	0
change / atm	–0.6x = –9	–0.6x		+3	+3
equilibrium/ atm	0.4 x	40 – 1.6x		3	3

Change in partial pressure of CO: $0.60\ x = (3)(3) = 9$ atm

Equilibrium pressure of CO = 0.4x

$= \left(\dfrac{0.4}{0.6}\right)(9)$

$= 6.0$ atm

1(c)(iv) Equilibrium pressure of $H_2 = 28 – 6 – 3 – 3$

$= 16.0$ atm

$K_p = \dfrac{P_{(CH_3OCH_3)}P_{(CO_2)}}{P_{(CO)^3}P_{(H_2)^3}}$

$= \dfrac{(3)(3)}{(6)^3(16)^3}$

$= 1.02 \times 10^{-5}\ atm^{-4}$ OR $9.65 \times 10^{-26}\ Pa^{-4}$

1(c)(v) When Ar(g) is added at constant volume, although the total pressure in the vessel increases, the partial pressure of the reactants and products remains the same. Hence there is no shift in position of equilibrium (or Q still equals to K) and the partial pressure of CH_3OCH_3 will remain the same.

1(c)(vi) When temperature increases, position of equilibrium (1) will shift left to favour the backwards endothermic reaction. As a result less products and more reactants will be formed and the K_p value decreases.

2(a)(i) The halogen radicals formed from Halon 1211 remove/combine with the radicals in the combustion reaction to terminate the chain reaction.

2(a)(ii) $Cl_2(aq) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$

HBr(g) dissolves in water to form $H^+(aq)$ and $Br^-(aq)$. Br^- can be oxidised/displaced by Cl_2 (a halide can be oxidised by the halogen above it in the group) to form $Br_2(aq)$, which is orange.

2(a)(iii) BE (H–C*l*) = +431 kJ mol^{-1} > BE (H–Br) = +366 kJ mol^{-1}

Since H–C*l* has a higher bond energy, it is harder to break the H–C*l* bond and the thermal stability of HC*l* is greater than that of H–Br.

2(b)

$Cl_2 + Fe \longrightarrow 2Cl^- + Fe^{2+}$ $\quad E^\ominus_{cell} = +1.36 - (-0.44) = +1.80\ V > 0$

$Cl_2 + Fe^{2+} \longrightarrow 2Cl^- + Fe^{3+}$ $\quad E^\ominus_{cell} = +1.36 - (+0.77) = +0.59\ V > 0$

Fe is oxidised by Cl_2 to form Fe^{3+}.

$I_2 + Fe \longrightarrow 2I^- + Fe^{2+}$ $\quad E^\ominus_{cell} = +0.54 - (-0.44) = +0.98\ V > 0$

$I_2 + Fe^{2+} \longrightarrow 2I^- + Fe^{3+}$ $\quad E^\ominus_{cell} = +0.54 - (+0.77) = -0.23\ V < 0$ (not spontaneous)

Fe is oxidised by I_2 to form Fe^{2+}.

Since Cl_2 can further oxidise Fe^{2+} to Fe^{3+} (or to a higher oxidation state) while I_2 cannot, this shows that Cl_2 is a stronger oxidising agent than I_2.

2(c)(i) Type of reaction involving CO_2: Reduction

The oxidation number of C decreases from +4 in CO_2 to +2 in HCOOH.

2(c)(ii) Cathode: $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$
Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$= -0.61 - (+1.23) = -1.84\ V$

$\Delta G^\ominus = -nFE^\ominus$
$= -(4)(96500)(-1.84) = +710240 = +710000\ J\ mol^{-1}$

Since $E^\ominus_{cell} < 0$ / $\Delta G^\ominus > 0$, it shows that the reaction in equation 1 is not spontaneous. Thus, a power supply is required for the reaction to occur.

2(d)(i) ①

CO_2 has <u>low solubility</u> in aqueous solution. The presence of gas diffusion electrode enables the <u>reaction</u> between CO_2 and H^+ to <u>occur without the need to dissolve CO_2</u> into the electrolyte.
OR
The presence of gas diffusion electrode <u>prevents CO_2 from dissolving in water</u> to form carbonic acid.
OR
The porous gas diffusion electrode will have a <u>larger surface area</u> for the reaction to take place and hence <u>increasing the rate of reaction</u> at the cathode.

②

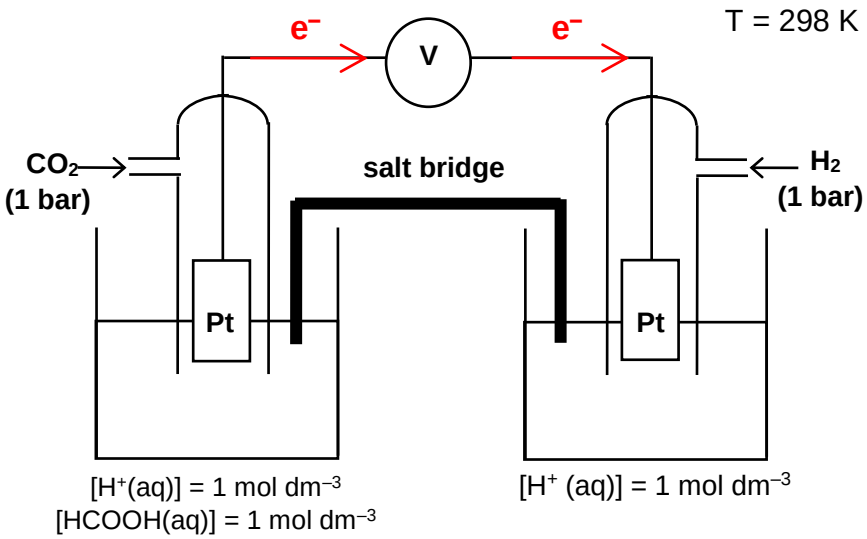
The *Nafion*™ membrane prevents HCOOH molecules to come into contact with the anode, thereby <u>preventing the oxidation of HCOOH</u>.

2(d)(ii) $CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$ $\qquad E^{\ominus} = -0.61$ V

A higher pressure of CO_2 will cause the <u>position of equilibrium to lie more to the right/ favour the forward reaction at the cathode</u>.

This results in a less negative $E(CO_2/HCOOH)$ value and the <u>E_{cell}</u> (which is equal to $E(CO_2/HCOOH) - E(O_2/H_2O)$) <u>will become less negative</u>, hence requiring a lower power supply.

2(e)



2(f)(i) Reduction half-equation: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$
Oxidation half-equation: $HCOO^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^-$

$3HCOO^- + 2MnO_4^- + OH^- \rightarrow 2MnO_2 + 3CO_3^{2-} + 2H_2O$

2(f)(ii) Amount of MnO_2 collected = $\frac{0.45}{86.9}$ = 0.005178 mol

Amount of $HCOO^-$ reacted = $\frac{3}{2}$ x 0.0051784 mol = 0.0077675 mol

Concentration of $HCOO^-$ reacted = 0.0077675 ÷ $\frac{30.00}{1000}$ = 0.259 mol dm^{-3}

3(a)(i) ①

Let the volume of $C_6H_5CH(OH)COOH$ (denoted by HA) and the volume of NaOH used be V dm^3.

Initial $n_{HA} = 0.25V$ mol Initial $n_{NaOH} = 0.125V$ mol

n_{A^-} formed $= n_{NaOH}$ reacted $= 0.125V$ mol

Unreacted $n_{HA} = 0.25V - 0.125V = 0.125V$ mol

$\Rightarrow$ The resultant solution is an acidic buffer at maximum buffering capacity.

pH of resultant solution = pK_a = –lg (3.89×10^{-4}) = 3.41

②

Initial n_{HA} = (0.25)(10/1000) = 0.0025 mol

Initial n_{NaOH} = (0.125)(20/1000) = 0.0025 mol = n_{A^-}

$\Rightarrow$ The resultant solution is a salt solution containing A^-.

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

$[A^-] = \frac{0.0025}{30}$ x 1000 = 0.0833 mol dm^{-3}

K_b of A^- = 10^{-14} / (3.89×10^{-4}) = 2.57 x 10^{-11} mol dm^{-3}

$$\left[OH^-\right] = \sqrt{K_b \times \left[A^-\right]} = \sqrt{2.57 \times 10^{-11} \times 0.0833} = 1.46 \times 10^{-6} \text{ mol dm}^{-3}$$

$$pOH = -\lg\left(1.46 \times 10^{-6}\right) = 5.83$$

pH = 14 – 5.83 = 8.17

3(a)(ii) Initial n_{HA} = (0.25)(10/1000) = 0.0025 mol

Initial n_{NaOH} = (0.125)(x/1000) = 0.000125x mol

n_{A^-} = 0.000125x mol

Unreacted n_{HA} = (0.0025 – 0.000125x) mol

$$\text{pH} = \text{p}K_a + \lg\left(\frac{[A^-]}{[HA]}\right)$$

$$3.89 = 3.41 + \lg\left(\frac{[A^-]}{[HA]}\right)$$

$$\lg\left(\frac{[A^-]}{[HA]}\right) = 0.48$$

$$\frac{[A^-]}{[HA]} = 10^{0.48} = 3.02$$

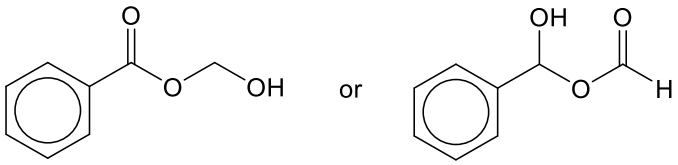
$$\frac{0.000125x / V}{(0.0025 - 0.000125x)/V} = 3.02$$

0.000125x = 3.02(0.0025 – 0.000125x)

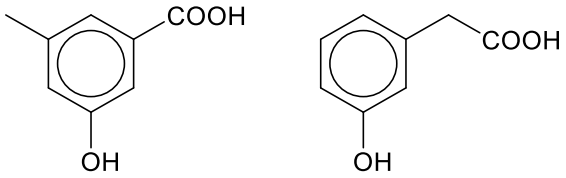
0.000125x + 0.0003775x = 0.00755

x = 15.0 cm^3

3(b)



X



Y **Z**

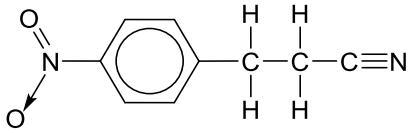
3(c) The <u>weaker</u> intermolecular <u>hydrogen bonds</u> in lactic acid require a much smaller amount of heat energy to overcome than the <u>strong ionic bonding</u> / <u>strong electrostatic forces of attraction</u> between oppositely charged ends of neighbouring zwitterions in alanine.

3(d)(i)

ala-met-his-asp
ser-phe-ala-met asp-his
his-ala-glu-thr
thr-glu

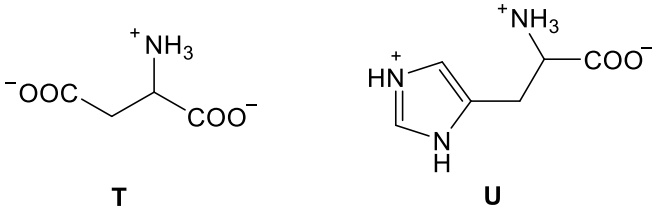
ser-phe-ala-met-his-asp-his-ala-glu-thr-glu

3(d)(ii) step 1: conc HNO_3, conc H_2SO_4, heat
step 2: ethanolic KCN, heat (under reflux)
step 3: H_2SO_4(aq), heat (under reflux)
step 4: Sn, conc HC*l*, heat (under reflux)



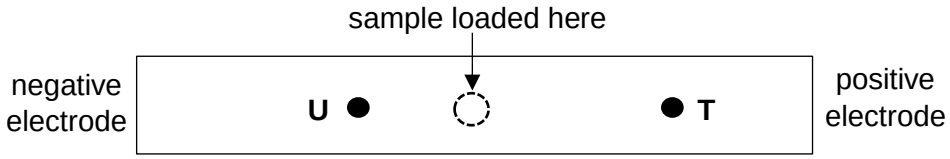
V

3(d)(iii)



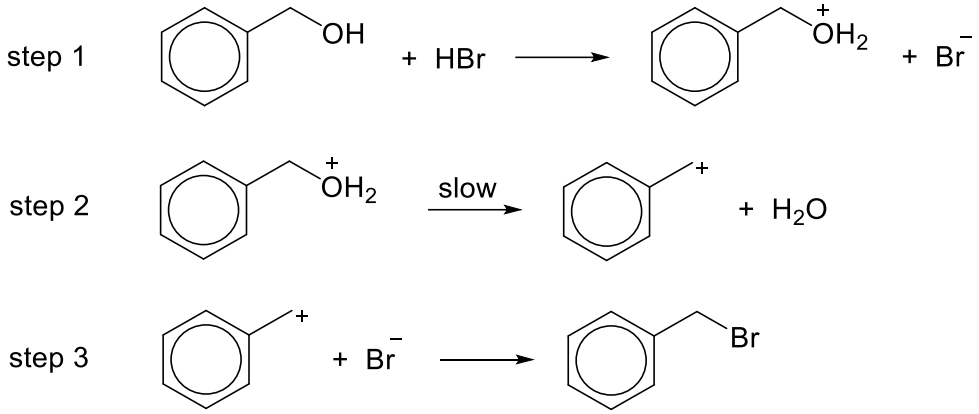
T **U**

3(d)(iv)



Section B

4(a)(i) Mechanism:



4(a)(ii) Test:
Add ethanolic $AgNO_3$ to each compound in a test-tube and heat in a hot water bath.

Observations:
Benzoyl bromide will give a (pale) cream ppt of AgBr almost immediately.
Benzyl bromide will give a (pale) cream ppt of AgBr after heating for some time.
Bromobenzene does not give any ppt.

4(b)(i) Carbanion **II** is more stable as the negatively charged carbon is bonded to two electron-withdrawing C=O groups while that in carbanion **I** is bonded to only one electron-withdrawing C=O group. Hence, the negative charge in carbanion **II** is more dispersed.

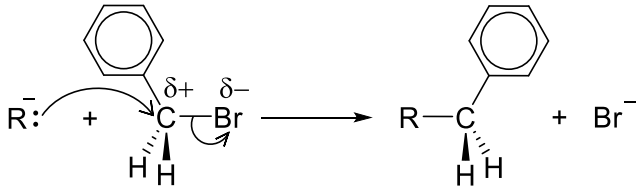
Also, the p orbital of the negatively charged carbon can overlap with the π electron cloud of the adjacent C=O, leading to the delocalisation of the negative charge into C=O. Carbanion **II** is more stable as the negative charge on carbon can delocalise into two C=O, while that in carbanion **I** delocalise into only one C=O.

4(b)(ii) LDA can act as a base as the lone pair of electrons on N atom is readily available for coordination with H^+.

However, LDA does not act as a nucleophile as the two bulky alkyl groups, $-CH(CH_3)_2$, poses steric hindrance to its attack on electron deficient carbon atoms/electrophile.

4(b)(iii) The hydroxide ion is both a strong base and a strong nucleophile as it does not contain any bulky groups. Hence, sodium hydroxide cannot be used in step 1 as the hydroxide ion can act as a nucleophile to attack the electron deficient carbon in C=O (of ketone and ester groups).

4(b)(iv) S_N2

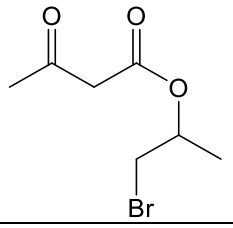
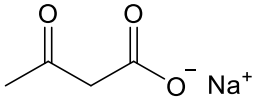
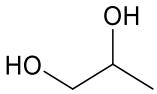


4(b)(v) identity of gas: CO_2

reagents and conditions: $H_2SO_4(aq)$ / $HCl(aq)$ / $HNO_3(aq)$, heat (under reflux)

4(c)

Information / Reaction	Deduction
P undergoes elimination to form only one alkene	• **P** is an <u>alkyl bromide</u>
P ($C_7H_{11}BrO_3$) does not react with $SOCl_2$	• No reaction with $SOCl_2$ • **P** has <u>no –OH and –COOH groups</u>
P ($C_7H_{11}BrO_3$) $\xrightarrow[\text{heat}]{\text{NaOH(aq)}}$ **Q** ($C_4H_5O_3Na$) + **R** ($C_3H_8O_2$)	• Basic hydrolysis of <u>ester group</u> and nucleophilic substitution of the alkyl bromide in **P** • **Q** is a <u>carboxylate salt</u> • **R** has <u>2 –OH groups</u>
P, **Q** and **R** give yellow ppt with hot aqueous alkaline iodine.	• Oxidation reaction (positive iodoform test) • **P** and/or **Q** have <u>$–COCH_3$</u> group • **R** has <u>$–CH(OH)CH_3$</u> group (Note: **Q** does not contain –OH group since **P** has no reaction with $SOCl_2$; **R** does not contain carbonyl group as its two O atoms are found in the 2 –OH groups)

P	**Q**	**R**
		

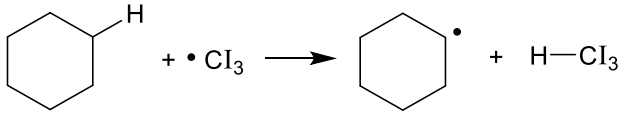
5(a)(i) Due to the small size of the O atoms, there is significant <u>repulsion between the lone pairs</u> on the two bonding O atoms, thus weakening the O−O bond.

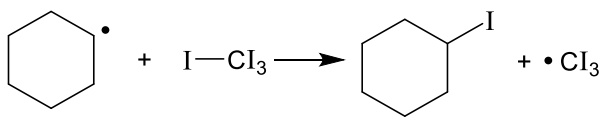
5(a)(ii) Initiation

$HO{-}OH \longrightarrow 2\ HO\bullet$

$HO\bullet + I{-}CI_3 \longrightarrow HO{-}I + \bullet CI_3$

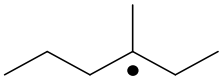
Propagation





5(a)(iii) Since the only function of the radical initiator, H_2O_2, is the <u>generation of the first $\bullet CI_3$</u> involved in the chain reaction in the system, it is used in trace amounts.

5(b)(i)

The alkyl radical intermediate formed,  , is trigonal <u>planar</u> about C-3 and Br_2 can attack C-3 from <u>either side</u> of the trigonal plane with <u>equal probability</u> resulting in the formation of 2 enantiomers in a 1:1 ratio.

5(b)(ii) Condensation

5(b)(iii) **G** and **H** are <u>no longer enantiomers</u> and have <u>different physical properties (m.p./b.p.)</u>. Hence, they can be separated by physical means such as fractional distillation or recrystallisation.

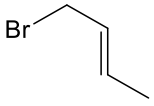
5(c) Cyclohexene undergoes electrophilic addition reaction with <u>Cl_2</u> in CCl_4 at room temperature and in the dark <u>without a Lewis acid catalyst.</u> The weak C=C π bond is easily broken and <u>only a weak $Cl^{\delta+}$ electrophile is required which can be generated by polarisation of Cl_2</u> by the electron rich C=C bond.

Benzene requires the use of a <u>Lewis acid</u> (e.g. $AlCl_3$) to generate a <u>stronger</u> Cl^+ <u>electrophile</u> since the reaction involves <u>disrupting the resonance stabilisation of benzene</u>.

5(d)(i) Add <u>2,4-DNPH</u> to each compound separately.
Intermediate **J** will give an <u>orange ppt</u> but not *o*-allylphenol.

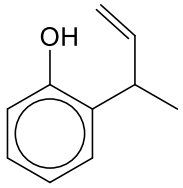
OR

Add <u>neutral $FeCl_3$(aq)</u> to each compound separately.
o-allylphenol will give a <u>violet complex</u> but not intermediate **J**.

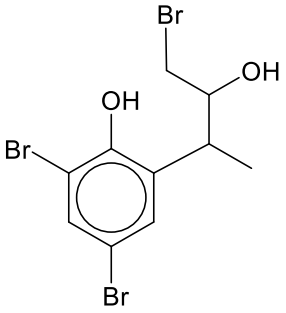
5(d)(ii) Step 1: Na / NaOH(aq), (room temperature)
Step 2: 

, heat (under reflux)
Step 4 : Br_2(aq), (room temperature)
Step 5 : $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat (under reflux)

5(d)(iii)



K



L