JURONG PIONEER JUNIOR COLLEGE 2019 JC2 H2 CHEMISTRY (9729) Preliminary Examination Paper 3 (Suggested Answers)

1 (a) For HI, violet fumes is observed.

 $E(H-Cl) = +431 \text{ kJ mol}^{-1}$; $E(H-I) = +299 \text{ kJ mol}^{-1}$

Since E(H-I) < E(H-Cl), H–I bond is weaker and is more easily broken than H–Cl bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).

OR

radius of Cl = 0.099 nm; radius of I = 0.133 nm

Since I has a larger radius than C_l , H–I bond is longer and weaker so it is more easily broken than H– C_l bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).

- **(b)** (i) $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
 - (ii) $E_{\text{cell}} = E_{\text{red}} E_{\text{ox}} (+1.23) (+1.36) = -0.13 \text{ V} < 0 \text{ (not energetically feasible)}$ Overall eqn: MnO₂ + 4H⁺ + 2Cl⁻ \rightarrow Mn²⁺ + 2H₂O

 $\Delta G = -zFE_{cell}$ where z = total number of electrons transferred per overall eqn

 $= -(2)(96500)(-0.13) = +25090 \text{ J ol}^{-1} = +25.1 \text{ kJ mol}^{-1}$

Since $\Delta G > 0$, the reaction is not energetically feasible (or not spontaneous) and thus unlikely to occur.

(iii) When concentrated HC*l* is used, [H⁺] is high and this causes the position of equilibrium of $MnO_2 + 4H^+ + 2e^- \ll Mn^{2+} + 2H_2O$ to shift right so as to react away some H⁺ ions. This makes $E(MnO_2/Mn^{2+})$ becomes more positive than +1.23 V such that the E_{cell} becomes positive and \therefore energetically feasible.

When concentrated HC*l* is used, [C*l*⁻] is high and this causes the position of equilibrium of $Cl_2 + 2e^- \ll 2Cl^-$ to shift left so as to react away some Cl^- ions. This makes $E(Cl_2/Cl^-)$ becomes more negative (or less positive) than +1.36 V such that the E_{cell} becomes positive and \therefore energetically feasible.

The continuous removal of Cl_2 gas from the reaction mixture as it is evolved shifts the position of equilibrium of $Cl_2 + 2e^- \ll 2Cl^-$ to the left to form back some Cl_2 . This makes $E(Cl_2/Cl^-)$ becomes more negative (or less positive) than +1.36 V such that the E_{cell} becomes positive and \therefore energetically feasible. (c) (i) Type of mechanism: electrophilic addition



- (ii) Propene can use its two π electrons to form a dative bond with H⁺ (or to accept a H⁺).
- (iii) Nucleophilic substitution
- (iv) p-p orbital overlap results in the delocalisation of lone pair on O of C-O into the π electron cloud of C=O, forming a partial double bond character in the C-O bond. This strengthens the C-O bond in -CO₂H, making it difficult to break. Hence, carboxylic acid is unreactive towards HC*l*.



- (e) (i) val-ala-val-ser-gly-arg-asn-leu-gly-val or leu-gly-val- val-ala-val-ser-gly-arg-asn or ser-gly-arg-asn-leu-gly-val- ala-val-ser
 - (ii) The lone pair on N_a is in the hybridised sp² orbital which is perpendicular to the p-orbitals of adjacent C=C and =C-N bonds. Hence, the lone pair on N_a is not delocalised and is available for protonation.

or

The lone pair on N_b is in the unhybridised p orbital which is parallel to the p-orbitals of adjacent C=N and C=C. Hence, the lone pair on N_b is delocalised and less/not available for protonation.



When enzyme is used in the decarboxylation reaction, it provides an alternative reaction pathway with lower activation energy, E_a '. This increases the number of reacting particles with energy $\geq E_a$ '.

Hence, the frequency of effective collisions increases and the rate increases.



2 (a) For ideal gas, the <u>volume of gas particles is negligible compared to the volume of gas/container</u>.

For ideal gas, there is <u>no/negligible forces of attractions between the gas particles</u>. For ideal gas, the <u>collision between the gas particle is perfectly elastic</u>.

(b) (i)
$$K_{\rm p} = \frac{{\rm p}_{\rm O_3}^2}{{\rm p}_{\rm O_2}^3}$$

(ii) Using
$$pV = nRT$$
 where V is in m³,

$$c = \frac{n}{V} \mod m^{-3} = \frac{p}{RT} \mod m^{-3} = \frac{p}{1000RT} \mod dm^{-3}$$
$$K_{c} = \frac{[O_{2}]^{2}}{[O_{3}]^{3}} = (\frac{p_{O_{2}}}{1000RT})^{2} \times (\frac{1000RT}{p_{O_{3}}})^{3}$$
$$= K_{p} \times 1000RT$$
$$= (6.1 \times 10^{-62})(1000)(8.31)(273+25) = 1.5 \times 10^{-55} \text{ Pa}^{-1} \text{ (shown)}$$

(iii) Since $K_p \ll 1$, it implies that the position of equilibrium $3O_2 \ll 2O_3$ lies on the far left and hence, the forward reaction hardly occurs and there are much less products than reactants at equilibrium.

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	3O ₂ (g)	\ll	2O ₃ (g)
initial conc. / mol dm-3	10.0 ÷ 4 = 2.50		0
change	-1.5 <i>x</i>		+ <i>x</i>
eqm conc. / mol dm ⁻³	2.50 – 1.5 <i>x</i>		x

$$K_{\rm c} = \frac{\left[O_3\right]^2}{\left[O_2\right]^3} = \frac{x^2}{\left(2.50 - 1.5x\right)^3}$$

Since $K_c \ll 1$, we can assume that $x \ll 2.50$ such that

 $1.5 \times 10^{-55} \approx \frac{x^2}{2.50^3}$ equilibrium [O₂], $x = 1.53 \times 10^{-27}$ mol dm⁻³

(c) (i)
$$3SO_2 + O_3 + 3H_2O \rightarrow 3H_2SO_4$$

(iv)

(ii) More energy is required to remove H⁺ from negatively charged ion HSO₄⁻ than from electrically neutral H₂SO₄ due to greater electrostatic force of attraction.
 Hence, HSO₄⁻ is a weaker acid than H₂SO₄.

(iii)		SO4 ²⁻	+	H+	\rightarrow	HSO_4^-
	initial amt	$0.200 \times \frac{10}{1000}$ = 0.002		$0.100 \times \frac{5}{1000}$ = 0.0005		0
	change	-0.0005		-0.0005		+0.0005
	final amt / mol	0.0015		0		0.0005

System: acidic buffer (mixture contain weak acid HSO₄⁻ and its salt SO₄²⁻)

$$pH = pK_a + lg \ \frac{[salt]}{[acid]} = [-lg(0.012)] + lg \left(\frac{0.0015}{0.0005}\right) = 2.40$$

(d) p-p orbital overlap results in the delocalisation of lone pair of electrons on O of phenol into benzene ring, making the lone pair less available for donation. Hence, phenol is a weaker nucleophile than alcohol (or less reactive towards nucleophilic reaction).

Reagent and condition: (1) NaOH(aq), room temperature (2), CH₃COC*l*(*l*), room temperature

(e) (i) 0 OH 0 Br



- (iii) excess (CH₃)₃NH₂, ethanol, heat in sealed tube
- (iv) If step 2 is carried out first, the phenolic group can undergo electrophilic substitution.
- (v) The N of salbutamol still possesses a lone pair and can function as a nucleophile for further substitution to occur.
- **3** (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
 - (ii) The maximum oxidation state is determined by the total number of 4s electrons and unpaired 3d electrons. Since the total number of 4s and unpaired 3d electrons increases from Sc to Mn and decreases from Mn to Zn, the maximum oxidation state increases from Sc to Mn then decreases from Mn to Zn.
 - (iii) $Sc^{3+}: 1s^2 2s^2 2p^6 3s^2 3p^6$

Fe³⁺: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵

Iron(III) salt are usually coloured due to d-d transition.

The presence of ligands causes the d orbitals to split into 2 different energy levels with relatively small energy difference, ΔE .

Radiation from the visible light region of the electromagnetic spectrum, corresponding to ΔE , is absorbed when an electron transits from a d orbital of lower energy to partially filled d orbital of higher energy.

Hence, iron(III) salts are coloured and the colour observed is the complement of the colours absorbed.

On the other hand, Sc³⁺ has no 3d electron and hence electron transition between d orbitals is not possible and radiation from visible light region is not absorbed.



(b) (i)

$$Cu^{2+} + 4Cl^{-} + Cu \ll 2[CuCl_2]^{-} ---(1)$$

 Cu^{2+} undergoes redox reaction with Cu foil to form a stable colourless $[CuCl_2]^-$ complex in the presence of Cl^- due to ligand exchange reaction.

The evaporation/removal of water due to heating causes the concentration of all aqueous species to increase while $[H_2O]$ remains relatively constant. This causes the position of equilibrium (1) to shift to the right side which has less concentration terms of aqueous species (excludes $[H_2O]$).

- (ii) CuC*l*
- (c) (i) Red-brown ppt of Cu_2O formed.



(ii) Since glucose has chiral carbons and has no plane of symmetry, it can exhibit enantiomerism.

Since there is restricted rotation around the C–C bond of the ring structure, it can exhibit cis–trans isomerism.

(iii) Let the percentage of α -glucose in the mixture be *x* % and that of β -glucose is (100-*x*) %.

$$\left[(+113.4) \times \frac{x}{100} \right] + \left[(+19.0) \times \frac{100 - x}{100} \right] = +52.2$$

% of α -glucose in the mixture, *x* = 35. 2 %

(iv) Disproportionation

- (a) (i) Electronegativity increases across the period and decreases down the group. Hence, beryllium and aluminium have similar electronegativity and have similar properties.
 - (ii) BeCl₂ has simple covalent/molecular structure while BeO has a giant ionic structure.

Less energy is required to overcome the weaker instantaneous dipole–induced dipole attraction between $BeCl_2$ molecules than that required for the stronger ionic bonds between Be^{2+} and O^{2-} .

Hence, the boiling point of $BeCl_2$ is lower than that of BeO.

(iii) BeCl₂ dissolves in water to give $[Be(H_2O)_4]^{2+}$ which hydrolyses (or react with water) to give an acidic solution. Due to the high charge density of Be²⁺, it can polarise and weaken the O–H bond in the coordinated H₂O molecules, releasing H⁺ into the solution.

Hence, a weakly acidic solution is formed and causes a beaker of litmus solution to change from purple to red.

Hydration: BeC l_2 + 4H₂O → [Be(H₂O)₄]²⁺ + 3C l^- Hydrolysis: [Be(H₂O)₄]²⁺ ≪ [Be(H₂O)₃OH]⁺ + H⁺

(b) (i) Since the A_r of Pb is 207.2, compound A can only contain 1 Pb.

% by mass of Pb in A = $\frac{207.2}{290} \times 100$ % = 71.45 %

% by mass of F in A = 100 - 71.45 - 3.08 = 25.47 %

element	Pb	Be	F
mass in 100 g / g	71.45	3.08	25.47
amount / mol	$\frac{71.45}{207.2} = 0.3448$	$\frac{3.08}{9.0} = 0.3422$	$\frac{25.47}{19.0} = 1.341$
simple ratio	1	1	4

Hence, the empirical formula of A is $PbBeF_4$ and thus, x = 1 and y = 4. or

mass of Be in one mol of PbBe_xF_y = $\frac{3.08}{100} \times 290 = 8.932$ g

mass of F in one mol of $PbBe_xF_y = 290 - 207.2 - 8.932 = 73.868$ g

element	Pb	Be	F
mass in 100 g / g	207.2	8.932	73.868
amount / mol	$\frac{207.2}{207.2} = 1$	$\frac{8.932}{9.0} = 0.9924$	$\frac{73.868}{19.0} = 3.888$
simple ratio	1	1	4

Hence, the empirical formula of A is $PbBeF_4$ and thus, x = 1 and y = 4.

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- (ii) $BeF_2 + 2KF \rightarrow K_2BeF_4$ (: anion is $BeF_4^{2^-}$)



- - (ii) A lCl_3 is acting as a catalyst since it reacted in step 1 and was regenerated in step 4.

 $AlCl_3$ is also acting as a Lewis acid since it accepted a lone pair of electrons from O atom of phenyl ethanoate via dative-bond formation.



(iv) Test: Add neutral FeCl₃(aq) to the reaction mixture.
 Obs: If 2–hydroxyacetophenone is formed, violet coloration is formed.
 or
 Test: Add Br₂(aq) to the reaction mixture.
 Obs: If 2–hydroxyacetophenone is formed, orange Br₂ decolourised.

Obs: If 2–hydroxyacetophenone is formed, orange Br_2 decolourised. or

Test: Add 2,4–DNPH to the reaction mixture.

Obs: If 2–hydroxyacetophenone is formed, orange ppt is formed. or

Test: Add alkaline $I_2(aq)$ to the reaction mixture and heat.

Obs: If 2-hydroxyacetophenone is formed, pale yellow ppt is formed.



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2-hydroxyacetophenone can form intramolecular hydrogen bond due to the close proximity of C=O and -OH groups, stabilising it and hence. 2-hydroxyacetophenone is likely to form in larger proportion.

- Electron-withdrawing -CO₂H reduces the electron density of benzene and makes the (d) benzene ring less electron-rich, causing phenyl ethanoate to be less reactive toward electrophilic attack. Hence, the rate of Fries rearrangement is slower for B compared to phenyl ethanoate.
- (i) Bond energy is the heat energy required when 1 mole of covalent bond in (a) gaseous phase is broken into gaseous atoms.

(ii)	Bonds broken			Bonds	formed	
	C=C	+610		3C–C	3(+350)	
	C–N	+305				
	Total	+915		Total	+1050	
$\Delta H_{\rm r} = (+915) - (+1050) = -135 \text{ kJ mol}^{-1}$						

- The ring strain in cyclopropane (or angle strain due to (iii) the rigid 3-membered ring structure of cyclopropane) weakens the C-C bond.
- (b) (i) Since E1 is a unimolecular reaction, it implies that the rate-determining step involves only one unit of a chemical species. From the description of E1 given, the first step is the rate-determining step and hence, the rate equation for E1 is rate = $k[(CH_3)_3CBr]$.

Since E2 is a bimolecular elementary reaction, it implies that it is one step mechanism (*i.e.* mechanism is the same as overall equation). Hence, the rate equation for E2 is rate = $k[(CH_3)_3CBr][OH^-]$.



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- (iii) Since the rate-determining step does not involve the base (or zero order w.r.t the base or only (CH₃)₃CBr is involved), changing CH₃CH₂O⁻ to (CH₃)₃CO⁻ would not change the rate of the E1 reaction.
- (c) (i) $CH_3CHBr(CH_3)_2 + OH^- \rightarrow CH_3CH(OH)(CH_3)_2 + Br^-$
 - (ii) E1 proceeds with an increase in entropy/disorderliness in the system since the number of particles increases from 2 mol to 3 mol but no change for S_N1 . Hence, ΔG of E1 becomes more negative with increasing temperature.
 - (iii) Benzyl chloride does not have adjacent C–H for elimination to occur.
 p–p orbital overlap results in the delocalisation of the positive charge on C⁺ into benzene ring, dispersing the positive charge and stabilising the carbocation.
 - (iv) Since the p K_a decreases from HF to HI, it implies that the position of equilibrium of HX \ll H⁺ + X⁻ lies increasingly more to the right.

Hence, the stability of leaving group X^- increases from F^- to I^- and the reactivity towards nucleophilic substitution increases from alkyl fluoride to alkyl iodide.