Dunman High School
2017 Year 6 H2 Chemistry
Preliminary Examination Paper 3 (Answer Scheme)
Section A

1 (a) (i)

1. The gas *particles* have negligible volume compared to the volume of the container.
2. There are no intermolecular forces of attraction between gas particles.

Its electron cloud size is larger hence volume of NO_2 molecules is significant compared to the volume of the gas, unlike H_2.

Both NO_2 and H_2 have simple molecular structure. Since NO_2 has stronger permanent dipole-permanent dipole interaction than instantaneous dipole-induced dipole interactions in H_2 *OR* NO_2 has a larger electron cloud size than H_2, the electron cloud of NO_2 is more polarisable and hence stronger intermolecular forces of attraction.

(ii) $pV = nRT = (m/M)RT$
$p = (m/V)(RT/M)$
$\frac{p}{\rho} = RT/M$
At 100 °C and very low pressure,
$RT/M = 110.3$
$M = (8.31 \times 373) / 110.3$
$= 28.1$ g mol^{-1}
$M_r = 28.1$

(iii) CO

(b) $NO_2 + SO_2 \rightarrow SO_3 + NO$
$NO + ½\ O_2 \rightarrow NO_2$

NO_2 catalyses by oxidising SO_2 to SO_3, while itself is reduced to NO. NO is rapidly re-oxidised to NO_2 by oxygen, regenerating the catalyst, NO_2.

$SO_3 + H_2O \rightarrow H_2SO_4$ *OR*
SO_3 dissolves in the water vapour in the atmosphere/ rain to form sulfuric acid, which causes acid rain.

(c) (i) Order w.r.t $[O_2]$ is zero as the graph of $[O_2]$ against time is a downward sloping straight line / the gradient of the line, i.e. rate of reaction, is constant with changing $[O_2]$.

When $[SO_2] = 0.8$ mol dm^{-3},
r_1, rate of reaction $= \left|\frac{0.04 - 0.05}{88}\right| = 1.13 \times 10^{-4}$ mol dm^{-3} s^{-1}
When $[SO_2] = 1.2$ mol dm^{-3},
r_2, rate of reaction $= \left|\frac{0.030 - 0.05}{80}\right| = 2.50 \times 10^{-4}$ mol dm^{-3} s^{-1}
$r_2/r_1 = 2.21 \approx 2.25$

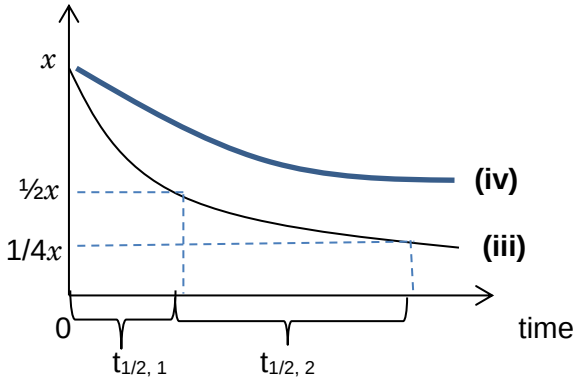
When $[SO_2]$ x 1.5 times, rate of reaction x 2.25 times, reaction is second order w.r.t $[SO_2]$.

(ii) rate = $k[SO_2]^2$

When $[SO_2]$ = 0.8 mol dm^{-3},
k = 1.77 x 10^{-4} mol^{-1} dm^3 s^{-1}

(k = 1.74 x 10^{-4} mol^{-1} dm^3 s^{-1}, if $[SO_2]$ = 1.2 mol dm^{-3})

(iii) $[SO_2]$ / mol dm^{-3}



2 (a) For hexane / cyclohexane mixture,

- Energy produced from instantaneous dipole – induced dipole (id-id) interactions between hexane and cyclohexane molecules after mixing
- is just sufficient to overcome id-id interactions between hexane molecules and between cyclohexane molecules before mixing.
- Thus no heat change is observed.

For hexane / ethanol mixture,

- Energy produced from weak id-id interactions between hexane and ethanol molecules after mixing
- is insufficient to overcome stronger hydrogen bonds between ethanol molecules before mixing.
- Thus heat is absorbed from the surroundings for mixing to occur.

(b) (i)

	bonds broken	bonds formed	ΔH / kJ mol^{-1}
step 1	1 C=C	1 C–C 1 C–I	(–350 – 240) + 610 = +20
step 2	1 H–Cl	1 C–H	–410 + 431 = +21

(ii)

- Only the free radical addition of HBr to an alkene is likely to occur since $\Delta H_{step\ 1}$, $\Delta H_{step\ 2}$ are all exothermic.

- This reaction is however unlikely to occur if HCl and HI were used.
- In each case, there is one propagation step which is endothermic — step 2 for HCl and step 1 for HI.

(iii) CH_3CHICH_3

2 (c) (i) **Q** : AgI
R : AgCl

- Reaction **I** is the nucleophilic substitution of a halogenoalkane in which C–*X* bonds (where *X* = C*l*, I) are broken to release X^- ions into solution to be precipitated as Ag*X*.
- Rate of substitution depends on the strength of C–*X* bond.

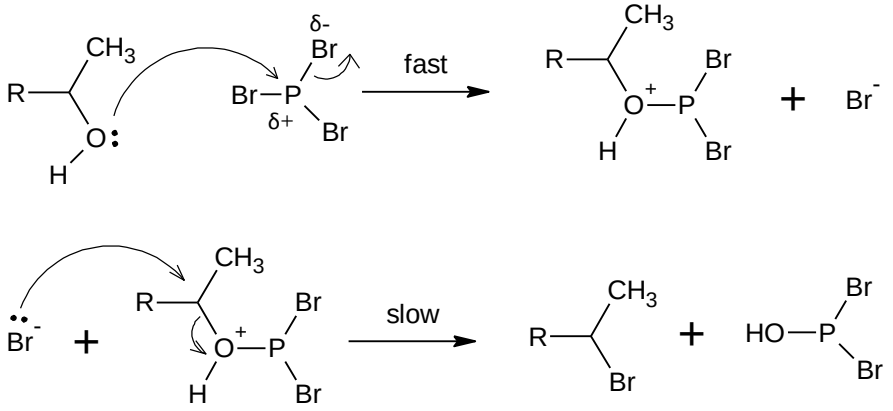
From the *Data Booklet*, BE(C–C*l*) : 340 kJ mol^{-1}
BE(C–I) : 240 kJ mol^{-1}

- C–I bond is weaker *OR* more easily broken than C–C*l* bond *OR* less amount of energy is needed to break C–I than C–C*l* bond.
- Thus, time taken for I^- ions to be released is shorter than that for Cl^- ions *OR* C–I bond is broken first *OR* AgI is precipitated first.

(ii)
- LiA*l*H_4 is a nucleophilic reducing agent *OR* is electron-rich.
- It attacks the electrophilic *OR* electron-deficient carbonyl C atom in carbonyl compounds, carboxylic acids and their derivatives but does not reduce electron-rich C=C bonds in alkenes.

(iii) Step **III**: I_2(aq) with NaOH(aq), heat

3 (a) (i)



3 (a) (ii) Lewis acid. PBr_3 accepts a lone pair of electrons from oxygen in the first step of the mechanism.

(iii) For phenol, the lone pair of electron on the oxygen atom is delocalised into the benzene ring and hence less available for donation and hence, phenol will be a weaker nucleophile, resulting in a relatively slower first step.

(iv) Phenol undergoes electrophilic substitution instead of addition to prevent the loss of its aromaticity (and resonance stability).

(v) Chemical test 1: Add $KMnO_4$ and dilute H_2SO_4, heat (in water bath)
Observation for phenol: Purple $KMnO_4$ does not decolourise
Observation for 2° alcohol used in (a): Purple $KMnO_4$ decolourises

OR

Chemical test 2: Add I_2 and NaOH, warm/heat (in water bath)
Observation for phenol: No yellow ppt forms
Observation for 2° alcohol used in (a): Yellow precipitate forms

OR

Chemical test 3: Add neutral FeCl_3(aq)
Observation for phenol: Violet colouration observed

Observation for 2° alcohol used in (a): No violet colouration observed

OR
Chemical test 4: Add $K_2Cr_2O_7$ and dilute H_2SO_4, heat (in a water bath)
Observation for phenol: Solution remains orange
Observation for 2° alcohol used in (a): Orange solutions turns green

3 (b) (i)

	$PCl_3(g)$ +	$Cl_2(g)$ ⇌	$PCl_5(g)$
Initial partial pressure / atm	2	1.5	0
Change in partial pressure / atm	–x	–x	+x
Eqm Partial pressure/ atm	2 – x	1.5 – x	x

Hence, (2 – x) + (1.5 – x) + x = 3.3
Partial pressure of PCl_5 at eqm, x = 0.2 atm

$K_p = \frac{(0.2)}{(2-0.2)(1.5-0.2)}$ = 0.0855 atm^{-1}

(ii) Since K_p is much less than 1, the position of the equilibrium lies to the left (or to the reactant side). This means that the forward reaction is not likely to be spontaneous and hence, ΔG should be positive.

(c) (i) $AsCl_5 + 4H_2O \rightarrow H_3AsO_4 + 5HCl$

Or

$AsCl_5 + H_2O \rightarrow AsOCl_3 + 2HCl$

$AsCl_5$ completely hydrolyses in water to produce a strong acid, HCl, which is responsible for the very low pH.

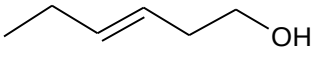
(ii)

OR

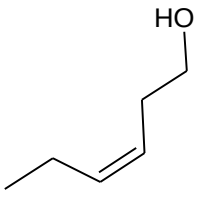
Bond angle: **<u>180°</u>**

4 (a) (i) Constitutional isomers are compounds with the same molecular formula but differs in structural formula.

(ii)



trans



cis

(b) **(i)** If Cu^{2+} is not complexed, it will form $Cu(OH)_2$ solid in alkaline medium and hence will not be able to react with the (aldehyde) functional group.

(ii) Cu^{2+} is a transition metal ion while K^+ is not.
Cu^{2+} has low lying partially–filled orbitals (or vacant subshell of low energy) which allows it to accept lone pair of electrons from tartrate ions to form a dative bond in complex formation.
K^+, however, does not low lying orbitals to form dative bonds with tartrate ligands.

(iii) $CH_2CCH_3(CH_2)_3CH(CH_3)CH_2CHO$ *OR*

$CH_2CCH_3(CH_2)_3CH_2CH(CH_3)CHO$ OR

$CH_2CCH_3(CH_2)_3CH(C_2H_5)CHO$

(iv) Amount of $Cu_2O = \frac{0.282}{143} = 0.00197$ mol

General equation (unbalanced):

$$X + 2\ Cu^{2+}(complexed) + OH^- \rightarrow Cu_2O(s) + products$$

$1\ X \equiv 2\ Cu^{2+}(complexed) \equiv 1\ Cu_2O(s)$

Amount of X present = 0.00197 mol
Mass of X present = 0.00197 x M_r of X
= 0.00197 x 154.0
= 0.3037 g
Percentage of compound X present = $\frac{0.3037}{2.0}$ x 100% = 15.2%

(v) From (iv), (max) mass of X vapourised/ present = 0.3037 g

Given that minimum concentration of X in the air to be "detectable" is 10 ppm,

i.e. 10 g of X in 1×10^6 g of air,

(Max) Mass of air for 0.3037 g of X to be detectable = $0.3037 \times (\frac{1 \times 10^6}{10})$
= 30 370 g
= 30.37 kg

Given that the density of air is 1.20 kg m^{-3},
Volume of air = $\frac{30.37}{1.20} = 25.3\ m^3$

(c) **(i)** Copper in solution Y has oxidation state of +1. Electronic configuration of Cu(I) is $1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}$

The ion has a fully–filled d orbitals (or no vacant or partially–filled d orbitals, hence a d electron from lower energy orbital cannot be promoted to a higher energy d orbital. Therefore, solution Y is colourless.

(ii) $CuCl_2 + Cu + 2HCl \rightarrow 2H[CuCl_2]$

OR

$Cu^{2+} + Cu + 4Cl^- \rightarrow 2CuCl_2^-$

(d) $Cu^{2+}(aq)$ which is $[Cu(H_2O)_6]^{2+}(aq)$ is blue in colour. When solid sodium chloride is added, it provides high $[Cl^-]$, causing H_2O ligands to be displaced by Cl^- ligands, forming $CuCl_4^{2-}(aq)$ complex, which is yellow in colour. When the following equilibrium is established, the presence of both $[Cu(H_2O)_6]^{2+}(aq)$ and $CuCl_4^{2-}(aq)$ makes the solution appear yellow-green.

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq) + 6H_2O$$

Upon addition of water, the equilibrium system is diluted. The aqueous reactants are diluted to a larger extent. By Le Chatelier's Principle, addition of water causes equilibrium position to shift to the left. Thus, the $[Cu(H_2O)_6]^{2+}(aq)$ ion dominates, reproducing the blue colour.

In the presence of sulfate ions, no ligand exchange reaction takes place, hence no change is observed as sulfate is a weaker ligand than H_2O.

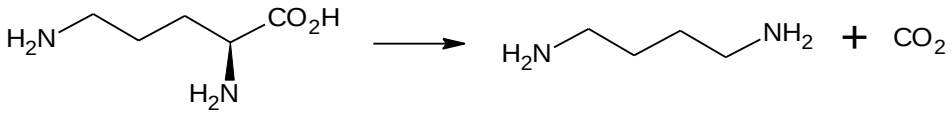
Section B

Answer **one** question from this section.

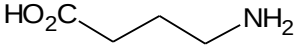
5 **(a)** **(i)** Gaseous by-product: CO_2

AND

Equation (stereochemistry not required):



(ii) Structure:



Name: 4-aminobutanoic acid

(iii) K_b is a measure of the strength/ basicity of a weak base.

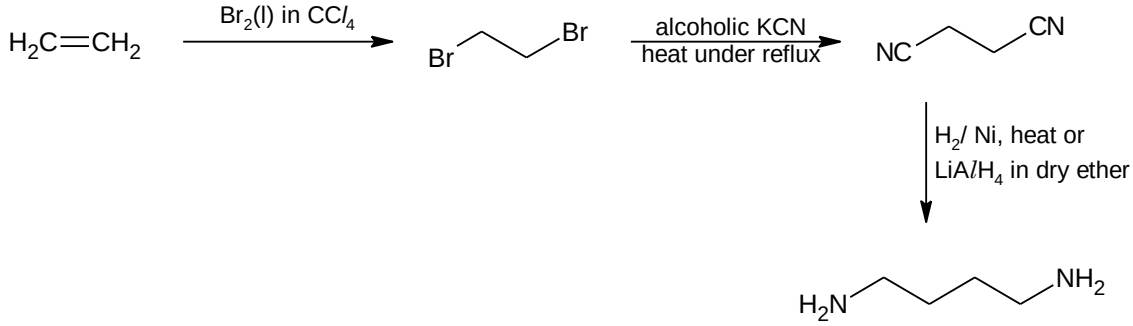
OR

K_b of a weak base, B = $\dfrac{[BH^+][OH^-]}{[B]}$

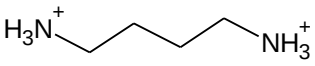
(iv) K_b: α-NH_2 of L-ornithine < R-NH_2 of L-ornithine

α-NH_2 of L-ornithine is closer to the electron-withdrawing $–CO_2H$/ $–CO_2^-$ group which decreases the availability of the lone pair of electrons on N atom of α-NH_2. Hence, α-NH_2 is a weaker base than R-NH_2 of L-ornithine.

5 (b)



5 (c) (i)



(ii) Ionic bonding

(d) (i) At the higher molar ratios, there is a large excess of unbound butane-1,4-diamine as binding sites of the DNA sample become saturated so energy change per mole of butane-1,4-diamine added is zero.

(ii) Endothermic since enthalpy change is positive when butane-1,4-diamine is added to the DNA sample.

(iii) ΔG < 0 since binding of butane-1,4-diamine with the DNA sample is spontaneous.

Since $\Delta G = \Delta H - T\Delta S$ and $\Delta H > 0$, $\Delta S > 0$ and $|T\Delta S| > |\Delta H|$ in order for $\Delta G < 0$.

(iv) The displacement of water molecules surrounding the DNA molecule disrupts the orderly arrangement which leads to an increase in disorder of the system.
OR
The moles of water molecules displaced from the DNA molecule are more than the moles of butane-1,4-diamine that bind with it, leading to an increase in disorder of the system.

5 (e) (i) $\Delta G^{\ominus} = -(8.31)(290)(\ln 4.88 \times 10^5)$
$= -315650$
$= -31\ 600\ \text{J mol}^{-1}$

(ii) Since $\Delta G^{\ominus}$ for butane-1,4-diamine is less negative than that for spermine, the binding constant K for butane-1,4-diamine is smaller than that for spermine.

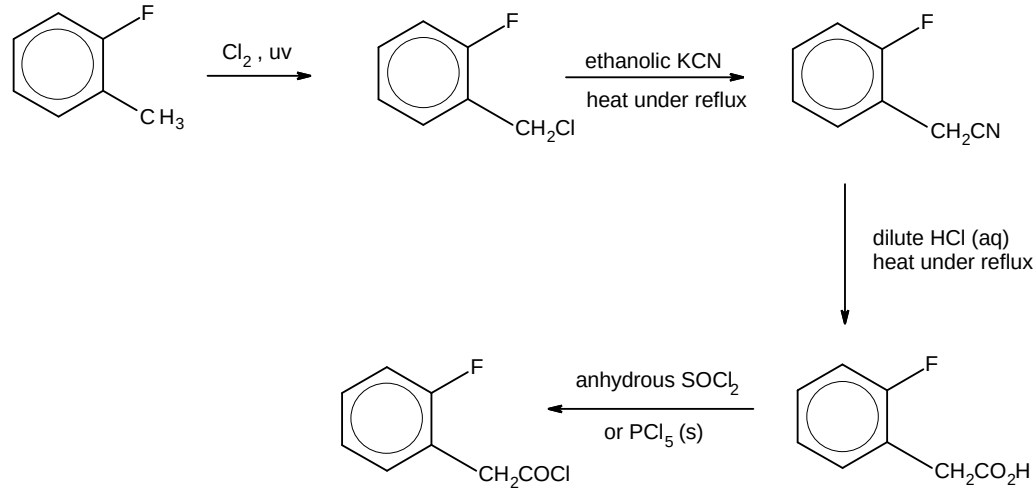
Hence butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

OR
$-2.62 \times 10^4 = -(8.31)(290)(\ln K)$

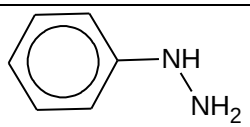
K = 52 671
= 5.27 x 10^4

Since the magnitude of K for butane-1,4-diamine is lower than that of spermine, butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

6 (a) (i)



(ii)

	reagent(s) and conditions	*type of reaction*
(I)	C_6H_6, (anhydrous) $AlCl_3$ or $FeCl_3$	Electrophilic substitution
(II)	 *OR* phenylhydrazine	Condensation
(III)	dilute HNO_3	Electrophilic substitution

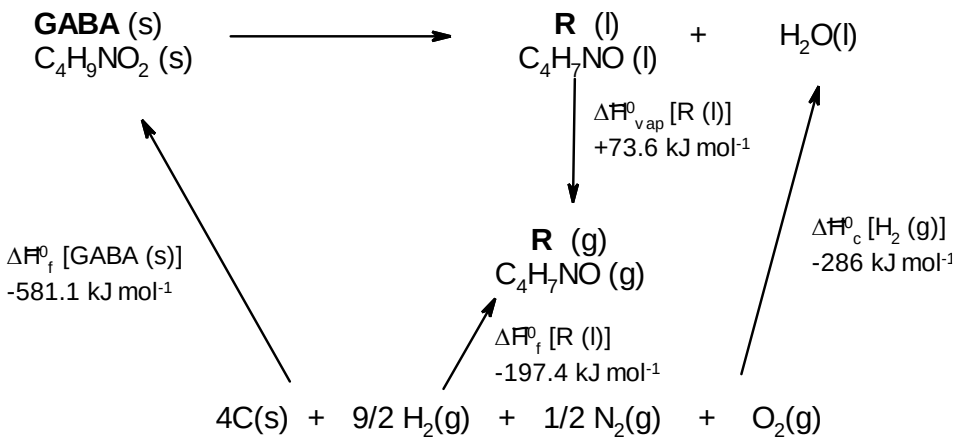
(iii) The half-life is too long and the patient will still be in a drowsy/ hangover state in the following day. / The effect of taking flunitrazepam at night will persist in the next day. / It takes too long for the sleep inducing effect of the drug to kick in. / There could be an overdose of the drug, due to its slow metabolism which results in accumulation of drug, if the patient continues to take drug on consecutive days.

(iv) Approximating $t_{½}$ of 23.5 h as 24 h or a day,

Day	Active mass absorbed / mg	Mass remained from previous day / mg	Total mass left / mg
1	0.8		
2	0.8	0.4	1.2
3	0.8	0.4 + 0.2	1.4
4	-	0.4 + 0.2 + 0.1	0.7
5	-	0.2 + 0.1 + 0.05	**0.35**

(b) **(i)** GABA exists as zwitterion in its natural form which results in strong electrostatic attraction between the zwitterions. Hence, it exists as solid at r.t.p.

(ii)



By Hess Law,

$\Delta H^{\ominus}_{\text{decomposition}}$ = –(–581.1) + (–197.4) – (+73.6) + (–286)

= +24.1 kJ mol^{-1}

(iii)