Raffles Institution
2012 Year 6 Preliminary Examination H2 Chemistry Paper 3
Suggested Solutions

1(a) **(i)** The melting point of lithium oxide is higher than that of sodium oxide.
As the Li^+ ion has a smaller ionic radius than the Na^+ ion, the Li^+ ion attracts the O^{2-} ion more strongly (or the lattice energy of Li_2O is more exothermic). Thus, a higher temperature is required to overcome the ionic bonds when lithium oxide is melted.

(ii) $6Na_2O + P_4O_{10} \rightarrow 4Na_3PO_4$

1(b) **(i)** $Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$ OR $CoO_2 + e^- \rightarrow CoO_2^-$

oxidation state of cobalt changes from +4 to +3

(ii) Graphite allows the migration of Li^+ ions to cobalt oxide.

(iii) Lithium reacts with water to form lithium hydroxide.

1(c) Mg reacts with water/steam to produce hydrogen.
As hydrogen is (highly) flammable, there will be a risk of explosion.

1(d) Chloride ions are smaller than bromide ions.
OR
Compared to the electrons of a bromide ion, the electrons of a chloride ion are closer to the nucleus.

Compared to an outer shell electron lost by a bromide ion, an outer shell electron lost by a chloride ion is more strongly held by the nucleus.

1(e) **(i)** A polydentate ligand forms more than one / two or more co-ordinate bonds with the central metal ion.
OR
A polydentate ligand donates more than one / two or more lone pairs of electrons to the central metal ion.

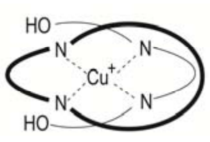
(ii) The number of product particles is greater than the number of reactant particles.
OR Disorderliness increases.
OR ΔS is positive.

$-T\Delta S$ is negative. $\Delta G = \Delta H - T\Delta S$. As $\Delta H = 0$, $\Delta G = -T\Delta S$. Thus, ΔG is negative.

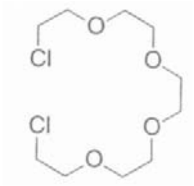
(iii) 6

(iv) The cyanide ion is strongly bonded to the Co^{2+} ion (by a co-ordinate bond).

1(f) **(i)** **Q**



(ii) **M**



(iii) The copper(I) ion, with a co-ordination number of 4, forms a stable complex, **Q**, with four nitrogen atoms (2 N atoms from **L** and 2 N atoms from **P**).
This complex allows a molecule of **L** to be located through the first ring, **P**, prior to cyclisation with **M**, to form the two interlocked rings.
OR
When the four nitrogen atoms form co-ordinate bonds with the Cu^+ ion to give a stable complex, **Q**, the two molecules, **L** and **P**, are locked in a particular spatial orientation in **Q**, allowing **M** to close up the ring afterwards.

2(a) **(i)** At cathode: $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$
At anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Overall: $2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2$

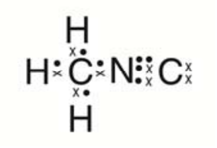
(ii) In addition to the electrolysis of water, energy has to be put in to drive the reduction of CO_2, a process which is not energetically feasible.

(iii) Methanoic acid can be further oxidised by $KMnO_4$.

(iv) $CH_3CN + 2H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$

(v) The other organic product is $CH_3NH_3^+$.

(vi)



2(b) **(i)** $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
$\Delta H = 2 \times 740 + (3 \times 436) - (3 \times 410) - 360 - (3 \times 460) = -182 \text{ kJ mol}^{-1}$

(ii) Methanol is a liquid. As bond energy data is for gaseous species only, the enthalpy change of reaction calculated in **(b)(i)** did not account for the enthalpy change of vaporisation of methanol.
OR
Bond energy values are average values.

(iii) At high pressure, gas molecules are compressed closer together, and hence, have significant intermolecular forces of attraction.

The smaller volume occupied by the gas also means that the actual volume occupied by the molecules becomes more significant in comparison to the volume of the container.

(iv) Heterogeneous catalysis

The presence of partially filled d orbitals in transition metals and their compounds allows for the ready exchange of electrons to and from reactants, thus facilitating the formation of weak bonds with the reactants.

In addition, the increase in surface concentration of the reactants increases the rate of reaction.

2(c) **(i)** Singlet form: $109.5° < \theta_1 < 120°$ (any one value)
Triplet form: $120° < \theta_2 < 180°$ (any one value)

(ii) The triplet form is more stable as electrons tend to occupy orbitals singly first so as to minimise inter-electronic repulsion.

(iii) nucleophilic addition

(iv) Air could be fed directly into the reaction system as a source of CO_2.

3(a) **(i)** The lone pair of electrons on nitrogen can be delocalised into the two benzene rings, making the lone pair unavailable to form a dative covalent bond with a H^+ ion.

(ii) $[H^+] = \sqrt{10^{-4.0} \times 0.10} = 3.162 \times 10^{-3}$ mol dm^{-3}
pH = $-\lg(3.162 \times 10^{-3}) = 2.50$

(iii) A buffer solution is one which is able to resist a change in pH (i.e. maintain an almost constant pH) upon the addition of a small amount of acid or base.

(iv) Let HA represent diclofenac.
$HA + NaOH \rightarrow H_2O + NaA$
$NaA \rightarrow Na^+ + A^-$
Amount of A^- = [400 / (400 + 600)] x 0.0500 = 0.0200 mol
Amount of HA unused = [600 / (400 + 600)] x 0.10 − 0.0200
= 0.0400 mol

$$pH = pK_a + \lg\frac{[A^-]}{[HA]} = 4.0 + \lg\frac{\frac{0.0200}{(400+600)\times10^{-3}}}{\frac{0.0400}{(400+600)\times10^{-3}}} = 3.70$$

(v) $HA + NaOH \rightarrow H_2O + NaA$
Amount of HA consumed = 0.0400 − 0.005 = 0.0350 mol
Amount of A^- produced = 0.0200 + 0.005 = 0.0250 mol

$$pH = pK_a + \lg\frac{[A^-]}{[HA]} = 4.0 + \lg\frac{\frac{0.0250}{(400+600)\times10^{-3}}}{\frac{0.0350}{(400+600)\times10^{-3}}} = 3.85$$

Change in pH = 3.85 − 3.70 = 0.15

3(b) **(i)** The quaternary structure of proteins refers to the spatial arrangement and association of polypeptide subunits.
Haemoglobin consists of two α subunits and two β subunits (or 4 subunits).
The subunits in haemoglobin interact with one another via ionic interactions, hydrogen bonds, disulfide bonds and van der Waals' interactions.

3(b) **(ii)** $Hb(H_2O)_4 + 4O_2 \rightleftharpoons Hb(O_2)_4 + 4H_2O$

oxyhaemoglobin

One haemoglobin molecule contains 4 subunits. Each subunit can bind to one oxygen molecule.
The oxygen molecule acts <u>as a ligand</u> and binds to the Fe^{2+} centre reversibly (or use "$\rightleftharpoons$" to show reversibility) through <u>dative covalent bonding</u>.

(iii) CO is a <u>stronger ligand</u> than O_2. Hence, CO <u>displaces</u> O_2 in oxyhaemoglobin almost irreversibly to form a more stable complex, carboxyhaemoglobin (HbCO). Consequently, this ligand exchange reaction cuts down the supply of oxygen to the body.

Allow the patient to inhale air which has a high concentration of O_2.

3(c) **(i)** $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$; units: $mol^{-1}\ dm^3$

(ii) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Amount of H^+ in 25.0 cm^3 of solution = Amount of OH^-
= 5.00 x (38.5 / 1000)
= 0.1925 mol

Amount of SO_3, y = amount of H_2SO_4 = ½ x amount of H^+ in 250 cm^3 solution
= ½ x 0.1925 x (250 / 25.0)
= 0.9625 mol

	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Initial amount/ mol	2		1		0
Change in amount/ mol	–y		–½y		+y
Equilibrium amount/ mol	2–y		1–½y		y

Amount of SO_2 = 2 − y = 2 − 0.9625 = 1.0375 = 1.04 mol
Amount of O_2 = 1 − (y/2) = 1 – (0.9625 / 2) = 0.51875 = 0.519 mol
Amount of SO_3= y = 0.9625 = 0.963 mol

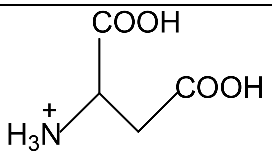
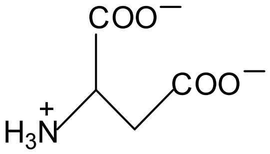
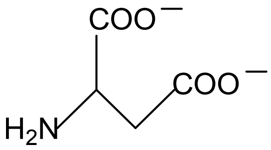
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\dfrac{0.9625}{3.60}\right)^2}{\left(\dfrac{1.0375}{3.60}\right)^2\left(\dfrac{0.51875}{3.60}\right)} = 5.97\ mol^{-1}\ dm^3$$

4(a) Phenylalanine exists predominantly as zwitterions in water. However, due to the close proximity of the two oppositely-charged groups, hydration is not efficient. Together with the hydrophobic phenyl group, phenylalanine is barely soluble in water.

In aqueous acids or alkalis, phenylalanine is able to form species which have a non-zero net charge. These charged species form strong ion-dipole interactions with water, so they have higher solubility in acids and alkalis.

4(b) **(i)** The carboxylic acid group that is nearer to the amino group is more acidic. The conjugate base of that carboxylic acid group is more stabilised due to the negative charge on O being more dispersed by the neighbouring electron-withdrawing amino group.

4(b) **(ii)**

pH 1	
pH 7	
pH 11	

(iii) Point **X**. At <u>isoelectric point</u>, the <u>sum of the charges of the species</u> in the solution is <u>zero</u>. Thus, the species present, $HOOCCH_2CH(NH_3^+)COO^-$, will not move when an electric field is applied.

4(c) **(i)** The **C1–N1** bond is shorter.
The **C1–N1** bond is formed by the overlap of an sp^2 hybrid orbital with an sp^3 hybrid orbital while the **C2–N2** bond is formed by the overlap of an sp^3 hybrid orbital with another sp^3 hybrid orbital. As the sp^2 hybrid orbital contains greater s-character, the bonding electrons are more strongly attracted by the nucleus of the carbon atom. Hence, a bond formed by sp^2-sp^3 overlap is shorter.
OR
The **C1–N1** bond is shorter.
The lone pair of electrons on **N1** can delocalise into the C=O functional group, resulting in a partial double bond character in the C–N bond.

(ii) $H_2NCO–CH_2–CHO$

(iii) $HOOC–CH_2CHO \xrightarrow[\text{room temp.}]{PCl_5} ClCO–CH_2CHO \xrightarrow[\text{room temp.}]{NH_3} H_2NCO–CH_2CHO$

4(d) **(i)** Denaturation is the process of disrupting the <u>secondary, tertiary, or quaternary structure</u> of proteins by breaking the <u>non-covalent interactions</u> (but including disulfide links) which hold these structures in their <u>native conformations</u>.

(ii) Any **<u>one</u>** of the following: Heat / Change the pH by adding strong acid or strong alkali / Add aqueous heavy metal ions such as $Ag^+(aq)$ or $Pb^{2+}(aq)$ / By mechanical agitation / Add organic solvents or detergents / Add enzymes
NOTE: Conditions for the hydrolysis of the hormone are **<u>not</u>** accepted.

4(e) **(i)** +5

(ii) The bulky $–NR_2$ groups around the N atom results in too much steric hindrance.
OR The central N atom does not have low-lying vacant orbitals to expand octet.

(iii) An acid-base reaction would take place instead.

(iv) nucleophilic substitution

5(a) **(i)** At a fixed temperature, add excess solid $Ca(OH)_2$ to water. Stir and filter the sample to obtain the saturated solution of $Ca(OH)_2$. To determine the concentration of hydroxide ions, titrate the saturated solution against a dilute mineral acid such as $HCl(aq)$, using methyl orange/phenolphthalein as indicator.

(ii)

	$Ca(OH)_2(s) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$2OH^-(aq)$
Initial conc^n		0	0
Equilibrium conc^n		s	2s

$K_{sp} = (s)(2s)^2 = 4s^3 = 6.5 \times 10^{-6}$
$[OH^-] = 2s = 0.02351$ mol dm^{-3}
$pH = 14 - (-\lg[OH^-]) = 14 + \lg 0.02351 = 12.37$

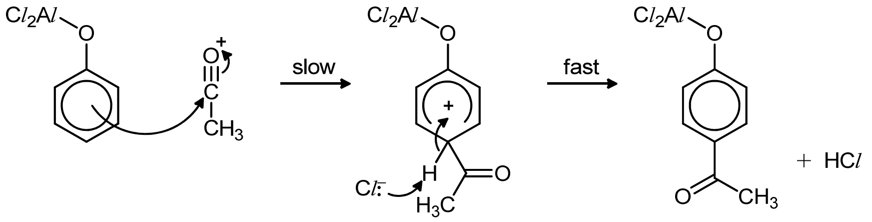
5(b) **(i)** The common gaseous product **V** is propanone, CH_3COCH_3.

(ii) $Mg(CH_3COO)_2(s) \rightarrow MgO(s) + CH_3COCH_3(g) + CO_2(g)$
$Ba(CH_3COO)_2(s) \rightarrow BaCO_3(s) + CH_3COCH_3(g)$

(iii) Mg^{2+} has a smaller ionic radius and higher charge density than Ba^{2+}.
Mg^{2+} polarises the ethanoate ion and distorts the C–O bond to a greater extent, leading to complete decomposition of magnesium ethanoate.

5(c) **(i)** +3

(ii)



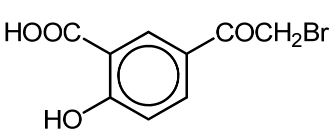
5(d) **(i)** NaOH deprotonates phenol to increase its nucleophilicity.

(ii) Na^+ chelates/attracts the oxygen atoms of phenol and CO_2, bringing the CO_2 electrophile closer to the 2- position for electrophilic attack.

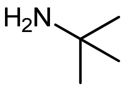
(iii) K^+ has a lower charge density than Na^+. Since K^+ has a lower tendency to be attracted to the CO_2 electrophile, the probability of 2- substitution is decreased.

5(e) **(i)** Step **I**: CH_3COCl and NaOH, followed by H^+ OR $(CH_3CO)_2O$, H^+
Step **II**: $AlCl_3$

(ii) **D**:



E:



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