HWA CHONG INSTITUTION
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 2

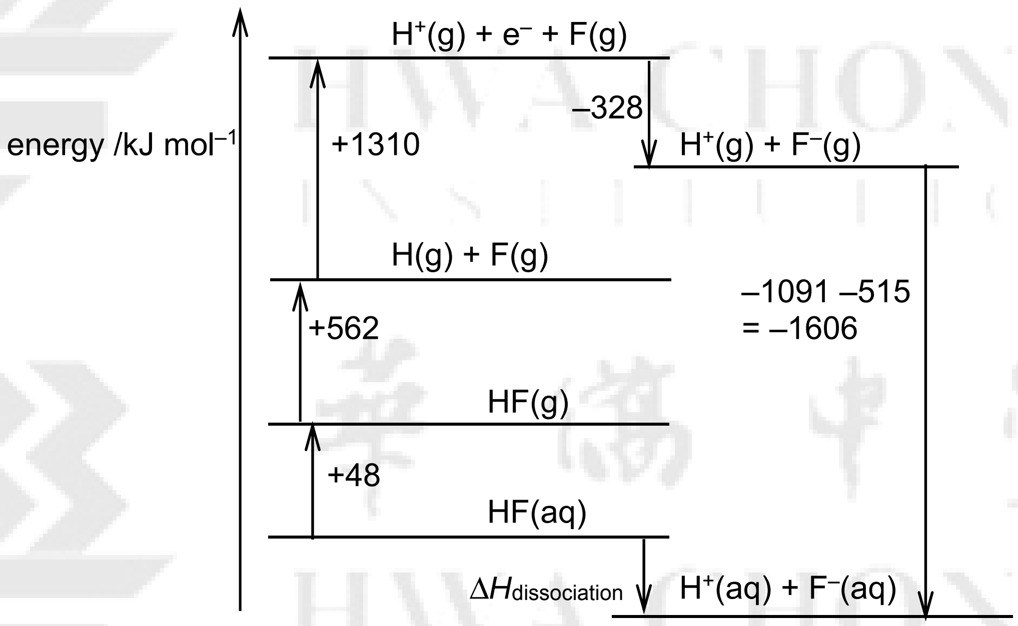
1 (a)

1. Thermal stability decreases from H–F to H–I **[1]**
2. Quote bond energy data:H–F +562 > H–C*l* +431 > H–Br +366 > H–I +299 kJ mol^{-1} and state that this H–X bond is broken during thermal decomposition. **[1]**

(b) (i) It is the heat released when 1 mol of gaseous F^- is dissolved in an infinite volume of water (or completely dissolved in water) at 298 K and 1 bar. **[1]**

$F^-(g) \rightarrow F^-(aq)$ **[1]**

(ii)



The steps to be drawn are:

1. +562 linking $HF(g) \rightarrow H(g) + F(g)$
2. +1310 linking $H(g) + F(g) \rightarrow H^+(g) + e^- + F(g)$
3. –328 linking $H^+(g) + e^- + F(g) \rightarrow H^+(g) + F^-(g)$
4. –1091 –515 linking $H^+(g) + F^-(g) \rightarrow H^+(aq) + F^-(aq)$

1 link correct ⇒ 1 mark
2-3 links correct ⇒ 2 marks
4 links correct ⇒ 3 marks

(iii) $\Delta H_{\text{dissociation}} = +48 + 562 + 1310 - 328 - 1606 = -14$ kJ mol^{-1}

[1] allow ecf from **(a)(ii)**

(c) **(i)** The hydrogen bond is formed because:

1. there is a H atom bonded to the highly electronegative F atom of one HF molecule **[1]**
2. and there is a lone pair on the F atom of another HF molecule **[1]**

(ii)

1. label δ+ δ– for the HF molecule that provides the protonic H
2. hydrogen bond link $H^{\delta+}$ atom of one HF molecule to lone pair on F atom of the second HF molecule
3. label H–F covalent bond 0.092 nm
4. label hydrogen bond 0.163 nm

[½] each

(d)

[1]

(e) **(i)**

1. Reaction between N_2 and H_2 gives fewer number of moles of gases (from 4 mol of gases to 2 mol) or fewer gas molecules **[1]**
2. Number of ways to distribute particles and/or energy decreases, disorder decreases. Hence entropy decreases **[1]**

(ii)

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$ **[1]**

(iii)

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	
initial mol	1	3		0	
change	–0.2	–0.2×3		+0.2×2	
eqm mol	0.8	2.4		0.4	Sum=3.6
eqm partial pressure	0.8/3.6 ×20 = 4.44	2.4/3.6 ×20 = 13.33		0.4/3.6 ×20 = 2.22	

$$K_p = \frac{(2.22)^2}{4.44(13.33)^3} = 4.69 \times 10^{-4}\ \text{MPa}^{-2}$$

[1] for all three equilibrium partial pressures
[1] for K_p value (allow ecf from partial pressures)
[1] for K_p units

Alternative working:

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	
initial MPa	x	$3x$		0	
change	$-0.2x$	$-0.6x$		$+0.4x$	
eqm MPa	$0.8x$	$2.4x$		$0.4x$	Sum=$3.6x$

$3.6x = 20$ MPa $\Rightarrow x = 5.556$

$K_p = \frac{(0.4x)^2}{(0.8x)(2.4x)^3} = 4.69 \times 10^{-4}$ MPa^{-2}

2 (a) Nucleophilic substitution
NaOH(aq), heat OR ethanolic KCN, heat OR ethanolic concentrated NH_3, heat (in sealed tube) **[1]**

Accept Elimination, ethanolic NaOH, heat
Accept (alkaline) Hydrolysis, NaOH(aq), heat

(b) (i) alcohol, phenol, carboxylic acid (any 2) **[1]**

(ii) The melting point of sodium, 98°C, is relatively low so it can easily be melted to react with the organic compound in the molten form. **[1]**

The standard reduction potential $E^\ominus(Na^+/Na) = -2.71$ V is very negative, which shows that sodium is a strong reducing agent / Na can easily be oxidised to Na^+, so sodium can react with / reduce the organic compound in the fusion reaction. **[1]**

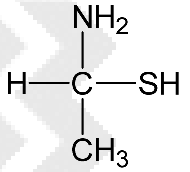
(c) (i) In the presence of ligands, the partially filled degenerate 3d orbitals of Fe^{2+} split into two different energy levels. The difference in the two energy levels, ΔE, is small, and falls within the visible region of the electromagnetic spectrum. There are vacancies in the higher energy d orbitals. An electron in a lower energy d orbital can absorb radiation in the visible spectrum and be promoted to the higher energy d orbital. This d-d electron transition gives rise to the colour. The violet colour seen is the complement of the absorbed colour which is yellow. **[3]**

(ii)

Element	Na	Fe	C	N	O	S
Percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4
A_r	23.0	55.8	12.0	14.0	16.0	32.1
Molar ratio **[1]**	1.178	0.294	1.475	1.764	0.294	0.293
Simplest ratio	4	1	5	6	1	1

Compound **A**: $Na_4FeC_5N_6OS$ **[1]**

(iii) NOS^- **[1]**

(d) 

$H-C(NH_2)(CH_3)-SH$ **[1]**

3 **(a)** **(i)** Hydrolysis **[1]**

(ii) No. of moles of N_2 formed = 2.50×10^{-3} mol
Max vol. of N_2 gas formed = $2.50 \times 10^{-3} \times 24.0 \times 10^{3}$ = 60 cm^3 **[1]**

[1] for finding and annotating the two half-lives in graph

[1] explanation: from the graph, $t_{1/2}$ is constant to about 14.5 min hence reaction is first order with respect to **D**.

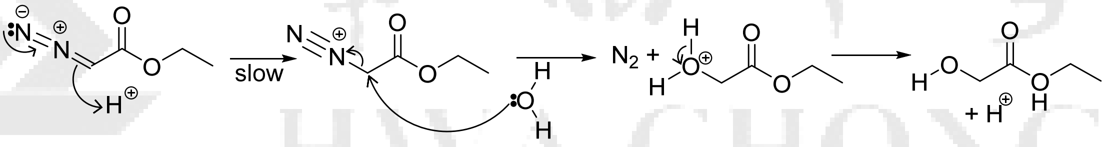
(iii) $k = \ln 2 / t_{1/2} = \ln 2 / 14.5 = \underline{0.0478\ min^{-1}}$ **[1m ans ; 1m unit]**

(b) **(i)**

expt	pH	Rate / mol dm^{-3} s^{-1}	[H^+] / mol dm^{-3}
1	2.0	2.69×10^{-2}	0.0100
2	2.3	1.35×10^{-2}	0.00500
3	2.4	1.07×10^{-2}	0.00398

[1]: correct order of H^+ with justification, e.g. comparing expt 1 and 2, when [H^+] increases by 0.01/0.005 = 2 times, rate increased by $2.69 \times 10^{-2}/1.35 \times 10^{-2}$ = 2 times. Reaction is first order with respect to H^+.

[1] Rate = k [H^+][**D**] ecf from order of H^+

(ii) 

[3] total

4 **(a)** **(i)** pH = 1.27
[H^+] = 0.0537 mol dm^{-3}
Let a = [$H_2C_2O_4$] used
$K_a = (0.0537)^2 / a - 0.0537$
a = 0.1027 mol dm^{-3} **[1]**

$$\frac{x}{100} \times \frac{1.50}{90.0} \times 1000 = 0.1027$$

x = $\underline{0.616\%}$ **[1]** with ecf

(ii) $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^{-} + OH^{-}$ **[1]**

[1] Explanation:
$C_2O_4^{2-}$ undergoes <u>hydrolysis to form OH^-</u>
$[OH^-] > [H^+]$ indicates pH is more than 7

(b) **(i)** ligand exchange reaction **[1]**
$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$ **[1]**

(ii) $H_2C_2O_4$ formed / neutralization / acid-base reaction when H_2SO_4 is added. The decrease in $[C_2O_4^{2-}]$ causes the position of equilibrium in equilibrium $[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$ to shift to the left **.**Hence, the presence of $[Fe(H_2O)_6]^{3+}$ gives rise to a pale yellow solution .

[1] mention $H_2C_2O_4$ formed/ neutralization / acid-base reaction occur <u>and</u> decrease in $[C_2O_4^{2-}]$
[1] equilibrium shift left, forming yellow $[Fe(H_2O)_6]^{3+}$

(iii) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77\ V$
$2CO_2 + 2H^+ + 2e \rightleftharpoons H_2C_2O_4$ $E^\ominus = -0.49\ V$

$2Fe^{3+} + H_2C_2O_4 \rightarrow 2Fe^{2+} + 2CO_2 + 2H^+$ **[1]**

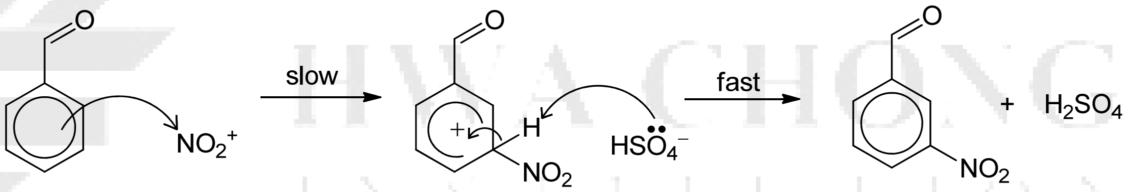
$E^o_{cell} = +1.26V > 0$ (spontaneous) **[1]**

The $Fe^{3+}(aq)$ formed oxidises $H_2C_2O_4$ to form CO_2 while itself is reduced to green $Fe^{2+}(aq)$ **[1]**.

5 **(a)** Electrophilic substitution **[1]**

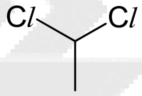
[2] mechanism

$2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$



(b) **(i)** **[1]** Idea along the lines of “2- or 4- chloro/bromobenzaldehydes can be formed despite –CHO being 3-directing”

(ii)
- restricted rotation about C=N bond **[1]**
- two different groups on C and on N on each end of the C=N double bond **[1]**

(c) **(i)**


[1]

(ii) **G**, $AlCl_3$ (or $FeCl_3$), heat **[1]**

(iii)

H: **[0.5]**

Step 3: I_2(aq), NaOH(aq), heat/warm **[0.5]** followed by dilute H_2SO_4 **[0.5]**

Step 4: $NaBH_4$ in methanol (or H_2, Ni, high pressure) **[0.5]**

OR

H: **[0.5]**

Step 3: $NaBH_4$ in methanol or $LiAlH_4$ in dry ether (or H_2, Ni, high pressure) **[0.5]**

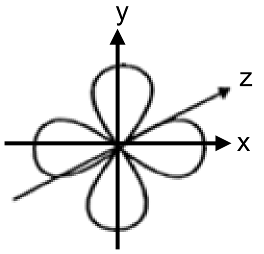
Step 4: 1) I_2(aq), NaOH(aq), heat/warm **[0.5]** followed by dilute H_2SO_4 **[0.5]**

(d) Oxidation half-equation: $C_6H_5CHO + 3OH^- \rightarrow C_6H_5CO_2^- + 2e^- + 2H_2O$ **[0.5]**

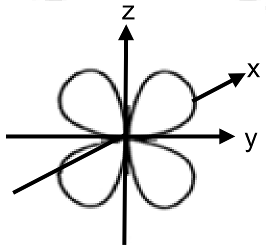
Reduction half-equation: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ **[0.5]**

Overall equation: $C_6H_5CHO + 3OH^- + 2[Ag(NH_3)_2]^+ \rightarrow C_6H_5CO_2^- + 2H_2O + 2Ag + 4NH_3$ **[1]**

(e) **(i)**



$d_{x^2-y^2}$ **[1]**



d_{yz} **[1]**

(ii) Highest energy d-orbital: d_{z^2} **[0.5]**

Lowest energy d-orbitals: d_{xy} and $d_{x^2-y^2}$ **[0.5]**

6 **(a)** **(i)** 24 **[1]**

(ii) $\Delta G^\ominus = -nFE^\ominus_{cell} = -(24)(96500)(0.85) = -1\,968\,600 \text{ J mol}^{-1} \approx -1970 \text{ kJ mol}^{-1}$
[1] allow ecf from **(a)(i)**

(iii) $E^\ominus_{cell} = +0.40 - E^\ominus(CO_3^{2-}/C_6H_{12}O_6) = +0.85$
$E^\ominus(CO_3^{2-}/C_6H_{12}O_6) = 0.40 - 0.85 = -0.45 \text{ V}$ **[1]**

(iv) $\Delta H^\ominus = 6(-670) + 12(-286) - [-1270 + 12(-230)] = -3422 \text{ kJ mol}^{-1}$ **[1]**

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$\Delta S^\ominus = [-3422 - (-1969)]/298 = -4.88 \text{ kJ mol}^{-1} \text{ K}^{-1}$ **[1]** allow ecf

(b) As concentration of glucose increases, $E(CO_3^{2-}/C_6H_{12}O_6)$ becomes **more negative** as **position of equilibrium** for the $CO_3^{2-}/C_6H_{12}O_6$ electrode reaction **shifts left** to **offset the increase in concentration of glucose**, this results in the initial increase of E_{cell}. **[1]**

Beyond an optimum glucose concentration, the **active sites** on the **surface** of nickel anode becomes **saturated** and further increase in glucose concentration will not lead to a decrease in the value of $E(CO_3^{2-}/C_6H_{12}O_6)$. Hence, value of E_{cell} remains constant. **[1]**

(c) **[1]** Glucose is a solid or used in aqueous form (liquid) while H_2 is a gas. Hence glucose will occupy a smaller volume for the same mass.

OR There is a risk of explosion for hydrogen gas as it is highly flammable while glucose is not as flammable.