## ANDERSON JUNIOR COLLEGE 2009 PRELIMINARY EXAMINATION HIGHER 2 CHEMISTRY PAPER 3 SOLUTIONS

- **1** (a) (i)  $CH_3COCH_3(I) + 4O_2(g) \rightarrow 3CO_2(g) + 3H_2O(I)$ 
  - (ii) Heat absorbed by water =  $0.70 \times 0.050 \times 1790 = 62.65 \text{ kJ}$ Let **m** be the maximum mass of water brought to boiling. Heat absorbed by water =  $\mathbf{m}c\Delta T = \mathbf{m}(4.20)(100-15) = 357 \text{ m J}$ 357 m = 62.650 $\mathbf{m} = \underline{175 \text{ g}}$
  - (iii) Heat loss to surroundings.
  - (iv) Since the forward reaction is accompanied by a decrease in number of moles of gaseous particles ( $\Delta n = -1$ ) and there is less disorder (or disorder decreases) which results in a negative entropy change.
  - (v)  $\Delta G^{\theta} = \Delta H^{\theta} T\Delta S^{\theta}$

Since  $\Delta S^{\theta}$  = negative and  $\Delta H^{\theta}$  = negative, a high temperature will give rise to an increase in  $|T\Delta S^{\theta}|$  such that  $|T\Delta S^{\theta}| > |\Delta H^{\theta}|$ ,  $\Delta G^{\theta}$  becomes positive and therefore reaction is not feasible.

(b) (i)  

$$CH_{3}COCH_{3}(l)$$
 $\Delta H^{\theta}_{at}$  (propanone)  
 $-248$ 
 $3C(g) + 6H(g) + O(g)$ 
 $3C(g) + 6H(g) + O(g)$ 
 $3C(s) + 3H_{2}(g) + \frac{1}{2}O_{2}(g)$ 
  
By Hess' Law,  
 $\Delta H^{\theta}_{at}$  (propanone) =  $\pm 3950$  kJ mol<sup>-1</sup>  
(ii)  $\Delta H^{\theta}at$  (propanone) =  $2BE(C-C) + 6BE(C-H) + BE(C=O)$   
 $= 2(+350) + 6(+410) + (+740)$   
 $= \pm 3900$  kJ mol<sup>-1</sup>

(iii)  $\Delta H^{\theta}_{vaporisation}$  (propanone) = + 3950 – 3900 = <u>+ 50 kJ mol<sup>-1</sup></u>



2 (a) (i) Nucleophilic substitution



(ii) Reaction II : LiAlH<sub>4</sub> in dry ether (or anhydrous) **OR** H<sub>2</sub>(g) over Pt catalyst Reaction III : (limiting)  $Cl_2$ , presence of uv light (or heat) Reaction IV : KOH in ethanol (or alcoholic KOH), reflux

(iii) 
$$H_2N$$
—CH—C $H_2NH_2$ 

- (b) <u>E</u> Heat with NaOH (aq) and acidify with excess dilute HNO<sub>3</sub>. Add AgNO<sub>3</sub> (aq). chloromethylamine : white ppt and E : cream ppt
  - <u>F</u> Add Br<sub>2</sub> (aq)
     F : decolourisation of brown Br<sub>2</sub> (aq).
- (c) The p-orbital on Cl can overlap with the  $\pi$  electron cloud of the aromatic ring, making the C–Cl bond stronger and less easily cleaved.
- (d) (i) Since 1 mol  $CH_3N=NCH_3 \equiv 1 \text{ mol } CH_3CH_3 \equiv 1 \text{ mol } N_2$

At any time t, if  $x \text{ cm}^3$  of CH<sub>3</sub>N=NCH<sub>3</sub> has reacted, then  $x \text{ cm}^3$  of CH<sub>3</sub>CH<sub>3</sub> and  $x \text{ cm}^3$  of N<sub>2</sub> would be formed.

Hence volume of  $CH_3N=NCH_3$  at any time *t*, *V* = initial total volume of gas – volume of  $CH_3N=NCH_3$  reacted + volume of  $CH_3CH_3$ formed + volume of N<sub>2</sub> formed

V = 600 - x + x + x = 600 - x (Shown)

(ii)	Time / s	0	210	420	860	1350	1800
	Vol of N <sub>2</sub> / cm <sup>3</sup>	0	6	10	15	18	19



Constant half-life at 390 s  $\Rightarrow$  1<sup>st</sup> order reaction

(iii) 
$$k = \ln 2 / t_{1/2} = \ln 2 / 390 = 1.65 \times 10^{-3} \text{ s}^{-1}$$



As shown on the diagram, when temperature increases, the number of reactant molecules with energy greater or equal to the activation energy,  $E_a$ , will increase. This results in an increase in the frequency of effective collisions and the rate of reaction increases.

- 3 (a) (i)  $2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$ 
  - (ii) No. of moles of Cd(OH)<sub>2</sub> = 3.65 / (112 + 17 + 17) = 0.025 mol
     No. of moles of electrons = 0.025 x 2 = 0.05 mol
     Total amount of charge = 0.05 x 96500 = 4825 C
     Time taken = 4825 / 3 = <u>1610 s</u> (26.8 min)
  - (iii) nickel electrode (anode) :  $OH^- \rightarrow O_2 + 2H_2O + 4e^$ cadmium electrode (cathode) :  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
  - (b) (i) The carbon electrode coated with  $MnO_2$  is the cathode, as the oxidation number of Mn changes from <u>+4 in MnO\_2</u> to <u>+3 in MnO(OH)</u>.
    - (ii)  $E_{red}^{\theta} = 1.60 0.76 = + 0.84 V$
    - (iii) No change in  $E^{\theta}_{cell}$  as the concentration of solid zinc remains the same
    - (iv) More environmentally friendly as cadmium is highly toxic (or no leakage / cheaper)
  - (c) Colour in Mn compound is due to d-d transition. In the presence of ligands, the partially filled 3d orbitals split into two levels with a small energy gap within the visible light energy. An electron from the lower energy level d-orbital can absorb energy from visible light and move to a vacant higher energy d-orbital. The colour of the manganese compound is the complementary colour to the one absorbed.
    - $Zn^{2+}$  has d<sup>10</sup> configuration, no vacant d orbitals for d-d transition.
  - (d) (i) KMnO<sub>4</sub> (ii) Disproportionation
    - (iii) No. of moles of  $MnO_2 = 0.174 / (54.9 + 16 \times 2) = 0.002 \text{ mol}$

No. of moles of compound H = 40/1000 x 0.5 x 1/5 = 0.004 mol

4

4 (a) 
$$[H^+] = 10^{-6.5} = 3.16 \times 10^{-7} \text{ mol dm}^{-3}$$
  
 $10^{-3.86} = \frac{(3.16 \times 10^{-7})^2}{[\text{lactic acid}]} \implies [\text{lactic acid}] = \underline{7.24 \times 10^{-10} \text{ mol dm}^{-3}}$ 

(b) (i) pH of buffer solution = pKa + 
$$\lg \frac{[\text{salt}]}{[acid]}$$
 = 3.86 +  $\lg \frac{0.200}{0.10}$  = 4.16

(ii) no. of moles of H<sup>+</sup> added = 
$$\frac{10}{1000} \times 0.10 = 1.00 \times 10^{-3} \text{ mol}$$

$$[\text{lactate}]_{\text{new}} = \frac{0.200 - 1.00 \times 10^{-3}}{1.0 + 10.0/1000} = 0.197 \text{ mol dm}^{-3}$$

$$[\text{lactic acid}]_{\text{new}} = \frac{0.10 + 1.00 \times 10^{-3}}{1.0 + 10.0/1000} = 0.100 \text{ mol dm}^{-3}$$

new pH of buffer solution = pKa + 
$$\lg \frac{[salt]}{[acid]}$$
 = 3.86 +  $\lg \frac{0.197}{0.100}$  = 4.15

(c) In order of <u>increasing</u> pH:

- (d) (i) dilute HNO<sub>3</sub>, room temperature
  - (ii) Electrophilic substitution



(e) (i) When the first trace of Fe(OH)<sub>2</sub> is formed,  $[Fe^{2^+}] [OH^-]^2 \ge K_{sp} (Fe(OH)_2)$   $(0.010) [OH^-]^2 \ge 1.6 \times 10^{-14}$   $[OH^-] = 1.265 \times 10^{-6} \text{ mol dm}^{-3}$   $pH = 14 + lg(1.265 \times 10^{-6}) = \underline{8.10}$ 

(ii) Maximum amount of  $Fe^{2+}$  can be extracted from the solution at the point when the first trace of Mg(OH)<sub>2</sub> is formed,

$$[Mg^{2^{+}}] [OH^{-}]^{2} \ge K_{sp} (Mg(OH)_{2})$$

$$(0.010) [OH^{-}]^{2} \ge 1.2 \times 10^{-11}$$

$$[OH^{-}] = 3.464 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = 14 - pOH = 14 + lg (3.464 \times 10^{-5}) = \underline{9.54}$$

$$[Fe^{2^{+}}] \text{ remaining in the solution} = \frac{1.6 \times 10^{-14}}{(3.464 \times 10^{-5})^{2}} = 1.333 \times 10^{-5} \text{ mol dm}^{-3}$$
the percentage of Fe<sup>2+</sup> remaining in the solution at this point
$$= \frac{1.333 \times 10^{-5}}{0.010} \times 100\% = \underline{0.133\%}$$

- 5 (a) (i) With <u>cold</u> aq NaOH:  $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$ With <u>hot</u> concentrated NaOH:  $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$ 
  - (ii) BrO<sub>3</sub><sup>-</sup> oxidizes hydrogen sulphide to sulfur (formed as yellow ppt); itself reduced to solution of bromine Br<sub>2</sub> (orange-red solution).
     Br<sub>2</sub> oxidizes iodide to iodine (dark brown solution) which precipitates out as black solids. (the brown solution is due to I<sub>3</sub><sup>-</sup> formed when I<sub>2</sub> dissolves in KI solution)

- (b) HI molecule has more electrons, thus instantaneous dipole-induced dipole attractions (i.d.i.d.) between HI molecules are stronger than between HC*l* molecules. Hydrogen bonding between HF molecules is stronger than i.d.-i.d. attractions between HC*l* molecules. Thus more energy needed to overcome the stronger intermolecular forces in HF and in HI than in HC*l*.
- $\begin{array}{lll} \text{(c)} & \text{BrF}_3: \text{T-shaped} & \text{changes to} \\ & \text{SbF}_5: \text{Trigonal bipyramidal} & \text{changes to} & \text{BrF}_2^+: \text{bent shape} \\ & \text{SbF}_6^-: \text{octahedral} \end{array}$
- (d) (i) Phenoxide ion formed is a stronger nucleophile than phenol which speeds up the rate of reaction.
  - (ii) C-C*l* bond is stronger than C-I bond
- (e) Electrophilic addition of 2 mol  $Br_2 \Rightarrow P$  is an diene (or it has two C=C double bonds)
  - Insoluble in aq NaOH  $\Rightarrow$  **P** is not a phenol
  - Reaction with Tollen's  $\Rightarrow$  **P** and **Q** have aldehyde groups
  - Oxidative cleavage of diene P produces R and S.
  - Triodomethane reaction with aq alkaline  $I_2 \Rightarrow R$  has  $CH_3CO$  group.

R is CH<sub>3</sub>COCO<sub>2</sub>H

**S** is :



• Thus, P is



• And reaction of P with Br gives structure Q

