

FULL NAME: .....

STUDENT ID: .....

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University of Canterbury

## Mid Year Examination and Test Period 2008

# ANSWERS

Prescription Number(s):	CHEM 111
Paper Title:	General Chemistry A

Time Allowed: 2.5 HOURS

Number of pages: 20 pages  
2 pages (formulae and periodic table)

Answer **ALL** questions

Total marks = 120

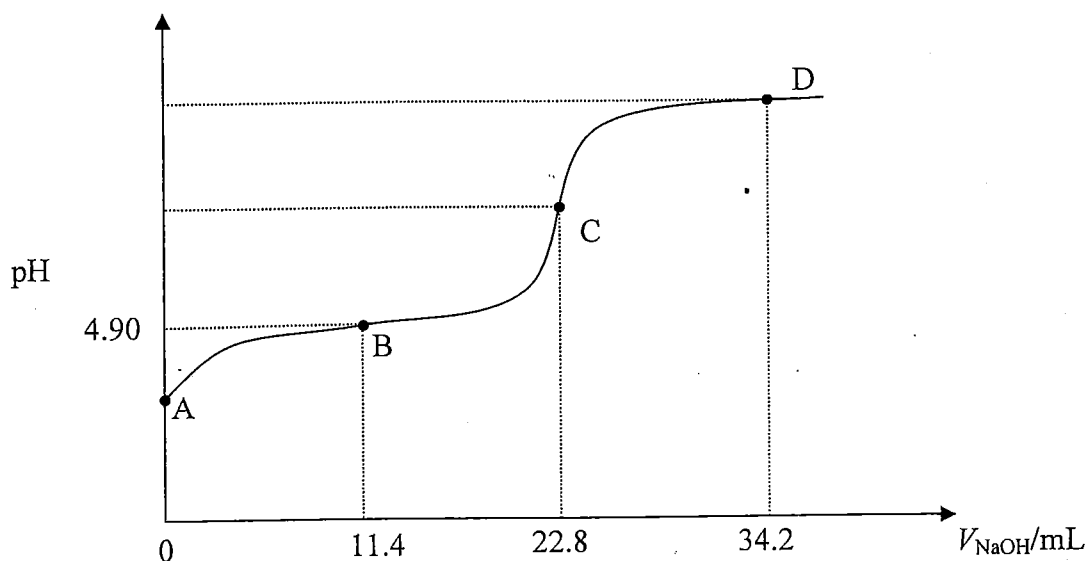
NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

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For examiners use only

1	2,3	4,5	6	7-11	12,13	Total/120
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1. (24 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 25.0 mL sample of a solution of weak acid, HA, of unknown concentration,  $C_{\text{HA}}$ , is titrated with standardised NaOH solution. The NaOH solution has a concentration of  $0.108 \text{ mol L}^{-1}$  and  $V_{\text{NaOH}}$  represents the volume in mL of NaOH which has been added. [Data:  $K_{\text{w}} = 1.00 \times 10^{-14}$ .]

(a) What pieces of laboratory equipment would be used to measure out:

(i) the volume of HA solution?

pipette

(ii) the added volume of NaOH,  $V_{\text{NaOH}}$ ?

burette

(b) On the figure above, clearly indicate and label the following:

(i) the equivalence point;

(ii) a buffer region.

(c) Calculate  $C_{\text{HA}}$ .

At equivalence point (ep), initial moles HA = moles  $\text{OH}^-$  added  
 $\Rightarrow C_{\text{HA}} V_{\text{HA, initial}} = C_{\text{NaOH}} V_{\text{ep}}$   
 $\Rightarrow C_{\text{HA}} = 0.108 \text{ mol L}^{-1} \times \frac{22.8 \text{ mL}}{25.0 \text{ mL}}$   
 $C_{\text{HA}} = 0.0985 \text{ mol L}^{-1}$

- (d) Using the given pH value for the solution at point B (4.90), calculate  $K_a$  (the acid ionisation constant) for HA.

At B, the half-equivalence point,  $n_{A^-} = n_{HA}$   
 Use this in buffer equation:  $pK_a = pH - \log_{10}(n_{A^-}/n_{HA})$   
 $= 4.90 - \log_{10}(1)$   
 $= 4.90$   
 $pK_a = -\log_{10} K_a \Rightarrow K_a = 10^{-pK_a} = 10^{-4.90} = 1.26 \times 10^{-5}$

- (e) What is the pH at point A?

pH is determined by:  $HA \rightleftharpoons H^+ + A^-$   
 $C_{HA} \quad 10^{-7} \quad 0$  (initial c in mol L<sup>-1</sup>)  
 $C_{HA-x} \quad 10^{-7}+x \quad x$  (equilibrium c in mol L<sup>-1</sup>)

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}} = \frac{(10^{-7}+x)(x)}{C_{HA-x}} \approx \frac{x \cdot x}{C_{HA}} \quad \text{since } x \gg 10^{-7}, \quad x \ll C_{HA}$$

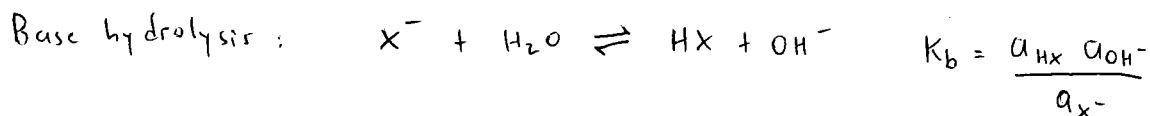
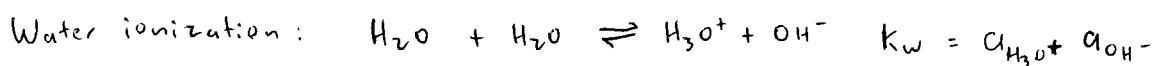
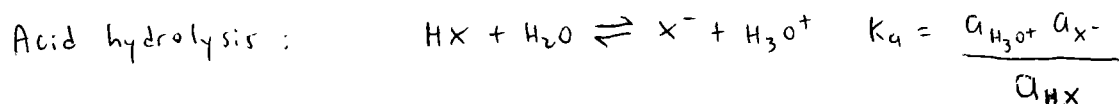
$$\Rightarrow x = \sqrt{K_a C_{HA}} = \sqrt{(1.26 \times 10^{-5}) \times (0.0985)} = 1.114 \times 10^{-3}$$

$$\Rightarrow pH = -\log_{10} x = 2.95$$

Fast answer:  $pH = \frac{1}{2} pK_a - \frac{1}{2} \log_{10} C_{HA} = 2.45 + 0.50 = 2.95$

- (f) Prove the **general result** that  $K_b$  (base ionisation constant) for the base  $X^-$  (i.e. conjugate base of the acid, HX) is given by

$$K_b(X^-) = K_w/K_a(HX)$$



$$\Rightarrow \frac{K_w}{K_a} = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_3O^+} a_{X^-}} = \frac{a_{HX} a_{OH^-}}{a_{X^-}} = K_b$$

(g) Calculate the pH at the equivalence point in the titration.

Titration reaction is  $HA + OH^- \rightarrow A^- + H_2O$

At equivalence point all HA has been converted into  $A^-$ .

Thus base hydrolysis occurs and determines pH:



$$C_{A^-} \quad \quad \quad 0 \quad \quad 10^{-7} \quad (\text{initial } c \text{ in mol L}^{-1})$$

$$C_{A^-} - x \quad \quad \quad x \quad \quad 10^{-7} + x \quad (\text{equilibrium } c \text{ in mol L}^{-1})$$

$$K_b = \frac{a_{HA} a_{OH^-}}{a_{A^-}} = \frac{x(10^{-7} + x)}{C_{A^-} - x} \approx \frac{x \cdot x}{C_{A^-}} \quad \begin{array}{l} \text{since } x \gg 10^{-7} \\ x \ll C_{A^-} \end{array}$$

$$\Rightarrow [OH^-] = x = \sqrt{K_b C_{A^-}}$$

$$K_b = \frac{K_w}{K_a} \quad (\text{see previous question})$$

$$= \frac{10^{-14}}{10^{-4.90}} = 10^{-9.1} = 7.94 \times 10^{-10}$$

$$C_{A^-} = \frac{n_{A^-}}{V_{\text{total}}} = \frac{\text{moles } OH^- \text{ added}}{V_{HA, \text{initial}} + V_{NaOH, \text{added}}} = \frac{C_{NaOH} V_{NaOH, \text{added}}}{25.0 \text{ mL} + 22.8 \text{ mL}}$$

$$= 0.108 \text{ mol L}^{-1} \times \frac{22.8}{47.8}$$

$$= 0.0515 \text{ mol L}^{-1}$$

$$\Rightarrow [OH^-] = 6.39 \times 10^{-6} \text{ mol L}^{-1}$$

$$\Rightarrow pOH = -\log_{10} [OH^-] = 5.19$$

$$\Rightarrow pH = 14 - pOH = 8.81$$

- (h) The endpoint of this titration could be detected using an indicator. Of the indicators listed below, which would be the most suitable? **Explain the reason for your choice.**

Indicator	$pK_a$ (indicator)
Ethyl red	4.9
Brilliant yellow	7.2
<i>o</i> -Cresolphthalein	9.0
2,4,6-Trinitrotoluene	12.3

Indicator changes colour when  $pH \approx pK_a(\text{indicator})$

Indicator should change colour at equivalence point.

At equivalence point,  $pH = 8.81$  (see previous question)

$\Rightarrow$  choose indicator with  $pK_a(\text{indicator}) \approx 8.81$

$\Rightarrow$  *o*-cresolphthalein most suitable.

- (i) What is the pH at point D?

Beyond the equivalence point, pH is determined by the excess

$$\text{of } OH^- : [OH^-] = \frac{\text{moles } OH^- \text{ in excess}}{\text{total volume of solution}}$$

$$= \frac{(\text{total moles } OH^- \text{ added}) - (\text{moles } OH^- \text{ reacted})}{\text{initial volume} + \text{volume added}}$$

$$= \frac{C_{NaOH} V_{NaOH, \text{ added}} - C_{NaOH} V_{NaOH, \text{ eq. pt.}}}{V_{HA} + V_{NaOH, \text{ added}}}$$

$$= 0.108 \text{ mol L}^{-1} \times \frac{(34.2 \text{ mL} - 22.8 \text{ mL})}{(25.0 \text{ mL} + 34.2 \text{ mL})}$$

$$= 0.0208 \text{ mol L}^{-1}$$

$$\Rightarrow pOH = -\log_{10} [OH^-] = 1.68$$

$$\Rightarrow pH = 14 - pOH = 12.32$$

2. (10 marks)

(a) Give brief definitions of the following thermodynamic terms:

(i) system;

The part of the universe that is of interest. The place where the "process" occurs

(ii) state function;

A function of the system whose value depends on the state of the system but not on how that state was achieved. For state function  $\Phi$

$$\Delta\Phi = \Phi_{\text{final}} - \Phi_{\text{initial}}$$

(iii) enthalpy/change;

Heat (transferred) at constant pressure

$$\Delta H = q_p$$

(iv) second law of thermodynamics;

A spontaneous process increases the entropy of the universe; an equilibrium process leaves the entropy of the universe unchanged

$$\Delta S_{\text{universe}} \geq 0$$

(v) third law of thermodynamics.

The absolute entropy of a perfect crystal at a temperature of 0K is equal to zero

$$S(\text{perfect crystal}; 0\text{K}) \equiv 0$$

3. (14 marks)

The data in the following table pertain to reaction (1) at 25°C:



substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
H <sub>2</sub> O(g)	-241.8	188.72
Cl <sub>2</sub> O(g)	80.3	266.1
HOCl(g)	-75.1	?

(a) Calculate  $\Delta H^\circ$  for reaction (1)

$$\begin{aligned} \Delta H^\circ &= 2\Delta H_f^\circ(\text{HOCl}(\text{g})) - \Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) - \Delta H_f^\circ(\text{Cl}_2\text{O}(\text{g})) \\ &= (-150.2 + 241.8 - 80.3) \text{ kJ mol}^{-1} = 11.3 \text{ kJ mol}^{-1} \end{aligned}$$

(b) Given  $K = 0.090$  for reaction (1), calculate  $\Delta G^\circ$  for the reaction at that temperature. [ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .]

$$\begin{aligned} \Delta G^\circ &= -RT \log_e K = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \\ &\quad \times \log_e(0.090) \\ &= 5.97 \text{ kJ mol}^{-1} \end{aligned}$$

(c) From your answers in (a) and (b), calculate  $\Delta S^\circ$  for reaction (1). (If you were unable to obtain answers, use the **incorrect** values  $\Delta H^\circ = 10.3 \text{ kJ mol}^{-1}$  and  $\Delta G^\circ = 5.0 \text{ kJ mol}^{-1}$ .)

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \Rightarrow \Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \\ \Delta S^\circ &= \frac{(11.3 - 5.97) \text{ kJ mol}^{-1}}{298 \text{ K}} = 17.9 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

- (d) From your answer in (c) and the data in the table, determine the absolute entropy of HOCl(g) at 298 K.

$$\Delta S^\circ = 2S^\circ(\text{HOCl(g)}) - S^\circ(\text{H}_2\text{O(g)}) - S^\circ(\text{Cl}_2\text{O(g)})$$

$$= 17.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

so

$$S^\circ(\text{HOCl(g)}) = \frac{1}{2} \times (17.9 \text{ J mol}^{-1} \text{ K}^{-1} + S^\circ(\text{H}_2\text{O(g)}) + S^\circ(\text{Cl}_2\text{O(g)}))$$

$$= \frac{1}{2} (17.9 + 188.72 + 266.1) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 236.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (e) Calculate  $\Delta G$  for reaction (1) under the following conditions:

$$P_{\text{H}_2\text{O}} = 0.24 \text{ atm}; \quad P_{\text{Cl}_2\text{O}} = 2.6 \times 10^{-3} \text{ atm}; \quad P_{\text{HOCl}} = 7.5 \times 10^{-3} \text{ atm}.$$

$$\Delta G' = \Delta G^\circ + RT \log_e \left( \frac{(a_{\text{HOCl}})^2}{a_{\text{H}_2\text{O}} a_{\text{Cl}_2\text{O}}} \right)$$

$$= \Delta G^\circ + RT \log_e \left( \frac{(P_{\text{HOCl}})^2}{P_{\text{H}_2\text{O}} P_{\text{Cl}_2\text{O}}} \right)$$

$$= 5.97 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}$$

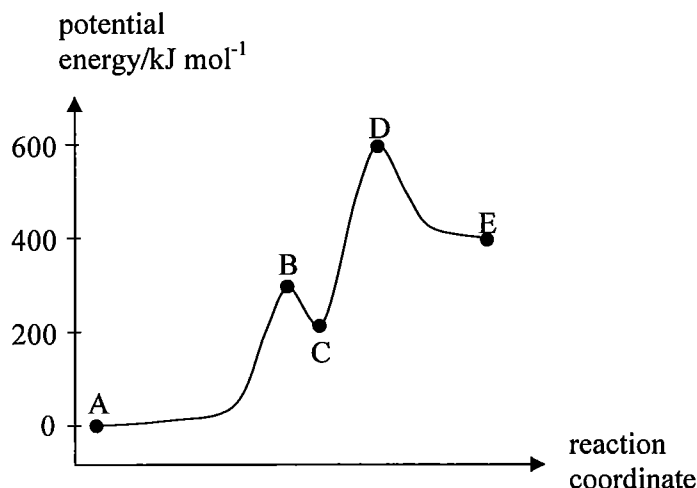
$$\quad \times \log_e \left( \frac{(7.5 \times 10^{-3})^2}{0.24 \times 2.6 \times 10^{-3}} \right)$$

$$= 5.97 \text{ kJ mol}^{-1} - 5.96 \text{ kJ mol}^{-1}$$

$$= 0.01 \text{ kJ mol}^{-1}$$

(nearly zero, so nearly at equilibrium)

4. (8 marks)



Using the figure above, answer the following:

(a) Is the overall reaction mechanism elementary or complex? Explain.

1 mark



Complex

1 mark

(for either

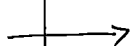


There is more than one elementary step (elementary reaction) involved

There are two transition states (B and D) and an intermediate

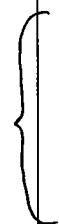
(b) Is the overall reaction endothermic or exothermic? Explain.

1 mark



Endothermic

1 mark



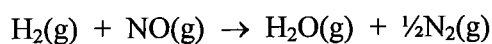
The potential energy of the products (C) is greater than that of the reactants (E).

(c) Indicate the point(s) (A-E) on the curve that correspond to:

- |                        |      |
|------------------------|------|
| (i) reactants          | A    |
| (ii) products          | E    |
| (iii) intermediates    | C    |
| (iv) transition states | B, D |

5. (12 marks)

The rate data in the following table were obtained at 700°C for the reaction



Expt	Initial concentration (mol L <sup>-1</sup> )		Initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )
	[H <sub>2</sub> ] <sub>0</sub>	[NO] <sub>0</sub>	
1	0.0100	0.0250	2.4 × 10 <sup>-6</sup>
2	0.0050	0.0250	1.2 × 10 <sup>-6</sup>
3	0.0100	0.0125	0.60 × 10 <sup>-6</sup>

(a) Give a general rate-law expression for the reaction in terms of a rate constant and the concentrations of the reactants.

2 marks

$$\text{Rate} = k [\text{H}_2]^\alpha [\text{NO}]^\beta$$

(b) From the data in the table, determine:

(i) the order of reaction with respect to H<sub>2</sub>;

2 marks

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k (0.0100)^\alpha (0.0250)^\beta}{k (0.0050)^\alpha (0.0250)^\beta} = 2^\alpha$$

$$= \frac{2.4 \times 10^{-6}}{1.2 \times 10^{-6}} = 2 \Rightarrow 2^\alpha = 2$$

First order w.r.t H<sub>2</sub>

$$\Rightarrow \alpha = 1$$

(ii) the order of reaction with respect to NO;

2 marks

$$\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{k(0.0100)^\alpha (0.0250)^\beta}{k(0.0100)^\alpha (0.0125)^\beta} = 2^\beta$$

$$= \frac{2.4 \times 10^{-6}}{0.6 \times 10^{-6}} = 4 \quad \Rightarrow 2^\beta = 4$$

$$\Rightarrow \beta = 2$$

2nd order w.r.t NO

(iii) the overall order of reaction.

2 marks

$$\text{overall order} = \alpha + \beta = 3$$

(c) From your answers in (b) and the data in the table, determine the value of the rate constant at 700°C, specifying its units.

2 marks

$$\begin{aligned} \text{Rate 1} &= k(0.0100)^1 (0.0250)^2 \text{ mol}^3 \text{ L}^{-3} \\ &= k \times 6.25 \times 10^{-6} \text{ mol}^3 \text{ L}^{-3} \\ &= 2.4 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \\ \Rightarrow k &= (2.4 \times 10^{-6} / 6.25 \times 10^{-6}) \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1} = 0.3840 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1} \end{aligned}$$

(d) From your results, is it possible to tell whether this reaction is elementary or complex? *Explain.*

1 mark

→ Yes. The reaction is complex

1 mark

The order of the reaction is not simply related to the stoichiometry

6. (18 marks)

(a) Use the following table of standard reduction potentials to answer the questions below:

Reduction Half-reaction	$E^\circ / V$
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89

(i) Which of the species in the table is the strongest oxidising agent?

①

 $\text{Au}^{3+}(\text{aq})$  - most +ve  $E^\circ$ 

(ii) Which of the species in the table is the strongest reducing agent?

①

 $\text{Sr}(\text{s})$  - most -ve  $E^\circ$ (iii) Which of the ions in the table will  $\text{Zn}(\text{s})$  reduce?

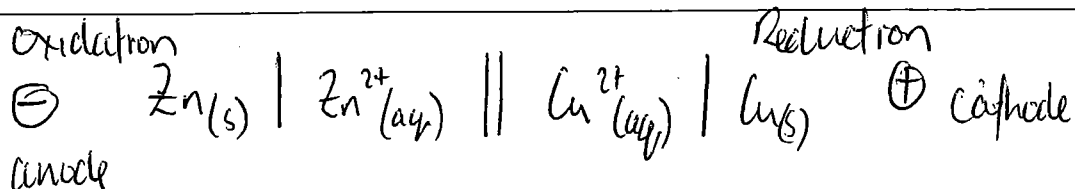
②

 $\text{Au}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  -  $E^\circ$  more +ve than  $\text{Zn}^{2+}/\text{Zn}$ 

(iv) Write down the conventional cell diagram for a cell that involves the zinc and copper half reactions above, and has a positive cell potential.

Calculate the standard cell potential for that cell.

③



②

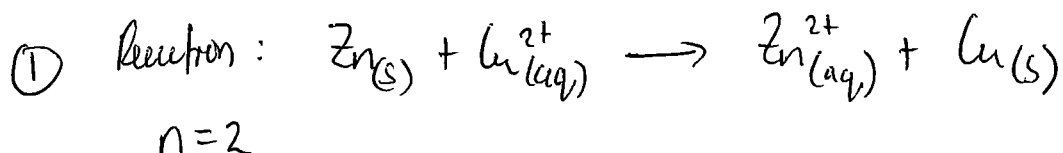
$$E^\circ = E_{\text{cathode}} - E_{\text{anode}} = E^\circ_{(\text{Cu}^{2+}/\text{Cu})} - E^\circ_{(\text{Zn}^{2+}/\text{Zn})}$$

$$= +0.34 - (-0.76)$$

$$= 1.10 \text{ V}$$

- (v) Calculate the equilibrium constant for the reaction of Zn(s) with Cu<sup>2+</sup>(aq).  
[R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>.]

$$\textcircled{1} \quad E^{\circ} = \frac{RT}{nF} \ln K$$



$$\textcircled{1} \Rightarrow 1.10 = 0.0128 \ln K$$

$$\ln K = 85.68 \quad \textcircled{1} \Rightarrow K = 1.6 \times 10^{37}$$

- (vi) Calculate the standard free energy change,  $\Delta G^{\circ}$ , for the reaction of Zn(s) with Cu<sup>2+</sup>(aq).

$$\textcircled{1} \quad \Delta G^{\circ} = -nE^{\circ}F$$

$$= -2 \times 1.10 \times 96489$$

$$\textcircled{2} \quad = -212,275 \text{ J mol}^{-1}$$

$$= -212 \text{ kJ mol}^{-1}$$

$$\Delta G^{\circ} = -RT \ln K$$

$$= -8.314 \times 298 \times 85.68$$

$$= -212,275 \text{ J mol}^{-1}$$

$$= -212 \text{ kJ mol}^{-1}$$

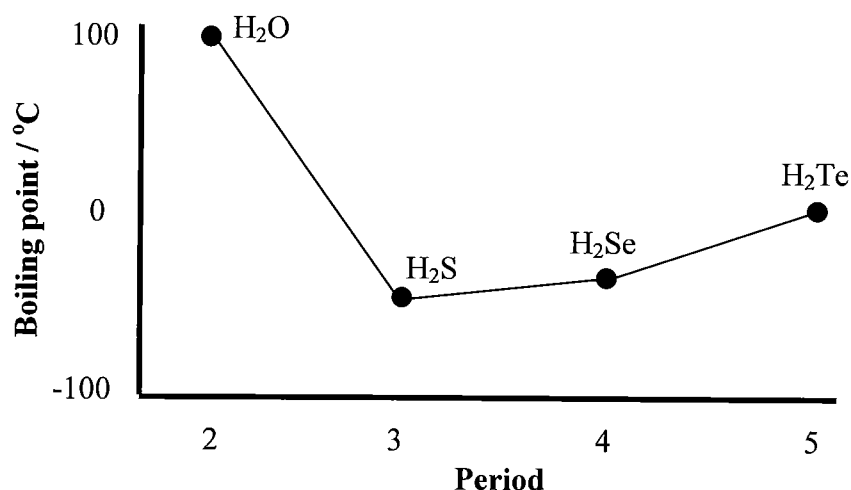
- (b) Give two methods that may be used to protect iron against corrosion. Briefly explain how they protect the iron from corrosion.

$\textcircled{2}$  Galvanising - Zn oxidised rather than Fe if in contact - protects until all Zn(s) consumed

$$E^{\circ}(\text{Zn}^{2+}/\text{Zn}) < E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$$

Paint - protects contact of metal from water and oxygen + ions.

7. (4 marks)



- (i) Explain why water exhibits the highest boiling point for the group 16 di-hydrogen compounds shown in the plot above.

H<sub>2</sub>O has a high dipole moment (unlike H<sub>2</sub>S - H<sub>2</sub>Te) and forms H-bonds. In order to boil water sufficient energy must be supplied to break the H-bonds which results in an elevation of the boiling point.

- (ii) Explain why the boiling points increase from H<sub>2</sub>S to H<sub>2</sub>Te.

Molecules increase in size and molecular or volume polarisability going from H<sub>2</sub>S to H<sub>2</sub>Se to H<sub>2</sub>Te. As the molecules become more polarisable the van der Waals force between them increases and this requires a higher energy input for boiling.

8. (1 mark)

$\text{Ba}(\text{OH})_2$  is soluble in water but  $\text{BaSO}_4$  is insoluble in water. Explain.

Solubility is lowest when cation and anion have same size (lattice energy is highest) and solubility is highest for salts where there is a large difference in size.

$\text{Ba}(\text{OH})_2$      $\text{Ba}^{2+}$  size  $>$   $\text{OH}^-$  size so soluble

$\text{BaSO}_4$      $\text{Ba}^{2+}$  size  $\approx$   $\text{SO}_4^{2-}$  size so insoluble

9. (4 marks)

The oceans, covering 72% of Earth's surface, exercise a moderating influence on the climate that limits high temperatures in Summer and low temperatures in Winter. Explain.

### Summer

Because water is hydrogen bonded (high heat capacity) as the temp increases the heat absorbed goes into breaking H-bonds with little rise in ocean temp (molecular speed) so T of oceans do not rise excessively over summer

### Winter

As temperature decreases heat is released in the oceans as H-bonds reform which precludes excessive fall in temperature.

10. (1 mark)

Circle the value in the list below that most closely equals the hydrogen bond strength in water.

A. 6 kJ mol<sup>-1</sup>

B. 25 kJ mol<sup>-1</sup>

C. 44 kJ mol<sup>-1</sup>

D. 102 kJ mol<sup>-1</sup>

11. (2 marks)

Answer the questions on the influence that hydrogen bonding has imposed on the value of the physical properties of water listed below by writing **I** for **increase** or **D** for **decrease** in the boxes provided.

Boiling Point

I

Vapour Pressure

D

Surface Tension

I

Density of ice

D

12. (12 marks)

At a temperature 400 K, the following reaction has a thermodynamic equilibrium constant of  $K = 0.0255$



(a) Give mathematical expressions for  $K$  in terms of:

(i) the equilibrium activities of the reaction components;

$$K = \frac{(a_{\text{H}_2})^3 a_{\text{N}_2}}{(a_{\text{NH}_3})^2}$$

(ii) the equilibrium partial pressures of the reaction components.

$$K = \frac{(P_{\text{H}_2})^3 P_{\text{N}_2}}{(P_{\text{NH}_3})^2}$$

(b) What are the units of a  $K$ ? *Explain your answer.*

$K$  is unitless. Despite appearances in (a) (ii) the true relationship is  
 $a_I \approx P_I/P^\circ$  where  $P^\circ = 1 \text{ atm}$

(c) At a temperature of 400 K, the equilibrium partial pressures of  $\text{NH}_3(\text{g})$  and  $\text{H}_2(\text{g})$  are, respectively, found to be  $P_{\text{NH}_3} = 1.00 \text{ atm}$  and  $P_{\text{H}_2} = 0.1 \text{ atm}$ . What is the equilibrium partial pressure of  $\text{N}_2(\text{g})$ ?

$$K = \frac{(0.1)^3 P_{\text{N}_2}}{(1.00)^2} = \frac{10^{-3} \times P_{\text{N}_2}}{1} = 0.0255$$

$$\Rightarrow P_{\text{N}_2} = 10^3 \times 0.0255 \text{ atm} = 25.5 \text{ atm}$$

(d) Each of the following cases, (i) to (iv), presents a *change* (stress) that may be applied to the system at equilibrium. You should use one of the following **letters** (A, B, C or D) to indicate how the system responds to the change:

- (A) Shift in the direction of the forward reaction.
- (B) No change.
- (C) Shift in the direction of the reverse reaction.
- (D) Cannot say.

If you answer **D** for a particular question, you should then indicate the **additional information** that you would require in order to decide whether A, B or C occurs.

(i)  $\text{N}_2(\text{g})$  is added at constant volume and temperature.

System response:  Additional information:

(ii) The volume of the system is increased at constant temperature.

System response:  Additional information:

(iii)  $\text{He}(\text{g})$  is added at constant volume and temperature.

System response:  Additional information:

(iv) The temperature is increased at constant pressure.

System response:  Additional information:

If  $\Delta H > 0$  then A

If  $\Delta H < 0$  then C

13. (10 marks)

- (a) Give a written explanation of the statement that a *system is in a state of dynamic equilibrium*.

There are processes occurring in both the forward and reverse directions with the same rates. The overall effect is no net change in the state of the system

- (b) By considering the reaction  $B + C \rightleftharpoons L + M$ , clearly distinguish between an *equilibrium constant* and a *reaction quotient*.

Reaction quotient

$$Q = \frac{a_L a_M}{a_B a_C}$$

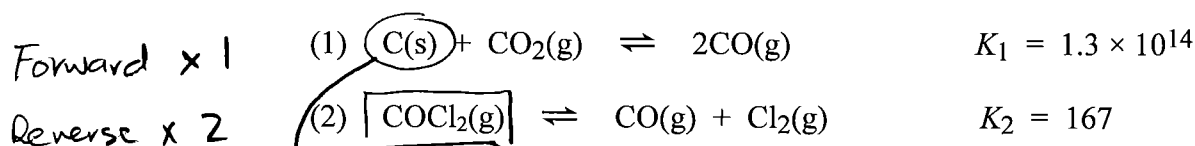
where the activities apply to any given state of the system

Equilibrium constant

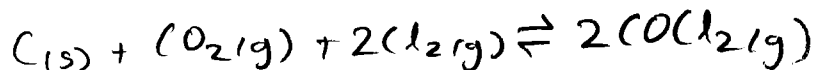
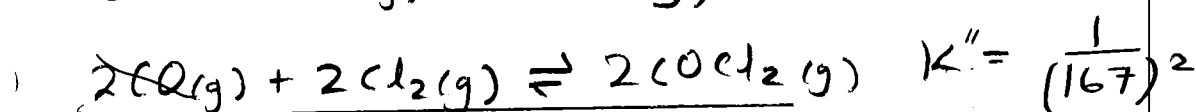
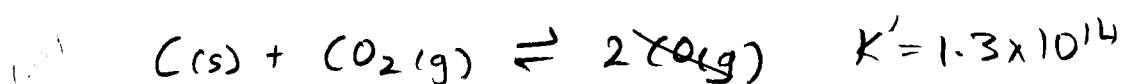
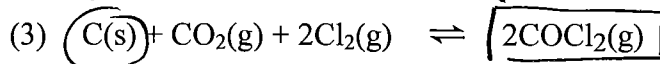
$$K = Q_{eq}$$

where the activities are those that apply to an equilibrium state.

- (c) At 1123 K the following reactions have the equilibrium constants shown:

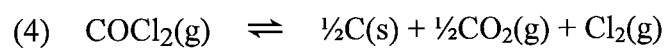


- (i) Calculate  $K_3$ , the equilibrium constant for reaction (3) at 1123 K:



$$K_3 = K' K'' = \frac{1.3 \times 10^{14}}{(167)^2} = 4.66 \times 10^9$$

- (ii) Write a mathematical expression (no calculations required) that relates the equilibrium constant  $K_4$  for reaction (4) to  $K_3$  for reaction (3) at the same temperature.



Reverse  $\times \frac{1}{2}$

$$K_4 = \frac{1}{(K_3)^{1/2}} = \frac{1}{\sqrt{K_3}}$$

**END OF PAPER**