University of Canterbury

Mid Year Examination and Test Period 2007

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

Time Allowed: 2.5 HOURS

Number of pages: 17

FAMILY NAME: .....

Answer **ALL** questions

GIVEN NAMES: .....

Total marks = 120

STUDENT ID#: .....

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

For examiners use only

1	2	3	4	5	6	7	Total

1. (22 marks)

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

	Reduction Half-reaction	$E°/V$
(i)	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.358
(ii)	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
(iii)	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
(iv)	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44

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

$Cl_2(g)$ as $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\ominus = 1.358\,V$

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

$Fe(s)$ as $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^\ominus = -0.44\,V$

(c) Which of the species in the table will $O_2(g)$ oxidise under acidic conditions?

$NO(g)$ ✗ $Fe(s)$ $E_+ - E_- > 0$

(d) Write down the conventional cell diagram for a cell involving the oxygen and iron couples ((ii) and (iv) in the list above) which has a **positive** standard cell potential.

$Fe(s) \mid Fe^{2+}(aq) \parallel O_2(g) \mid H^+(aq) \mid Pt(s)$

Question 1 continued on following page

Question 1 continued

(e) Calculate the standard cell potential for the cell in (d).

$$E^{\ominus}_{cell} = E^{\ominus}_{+} - E^{\ominus}_{-} = E^{\ominus}_{O_2|H_2O} - E^{\ominus}_{Fe^{2+}|Fe}$$

$$= 1.23 - (-0.44) = 1.67\ V$$

(f) Calculate the standard free energy change, ΔG°, for the reaction of $O_2(g)$ with Fe(s) in acid.

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

oxidn $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ (×2)

redn $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

$n = 4$

$\Delta G^{\ominus} = -4 \times 96485\ C\,mol^{-1} \times 1.67\ V$

$= -644.5\ kJ\,mol^{-1}$

(g) Calculate the thermodynamic equilibrium constant, K, for the reaction of $O_2(g)$ with Fe(s) in acid.

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

$$-644500 = -8.314 \times 298 \times \ln K$$

$$\ln K = 2.6013 \times 10^2$$

$$K = e^{260.13}$$ ANS

$$E^{\ominus} = \frac{0.0591}{n} \log_{10} K$$

$$1.67 = 1.4775 \times 10^{-2} \log_{10} K$$

$$\log_{10} K = 1.1303 \times 10^2$$ ANS

Question 1 continued on following page

Question 1 continued

(h) Write down the Nernst equation for an electrochemical cell in which the cell reaction is the reaction of $O_2(g)$ and Fe(s) under acidic conditions.

$$E = E^{\ominus} - \frac{RT}{nF} \ln \frac{a_{Fe^{2+}}^2}{a_{O_2} a_{H+}^4}$$

$E^{\ominus} = 1.67 V$

$n = 4$

(i) Describe one method of corrosion prevention and explain how it relates to the equation in part (h).

Galvanize with Zn, Zn more easily oxidised than Fe as Zn acts as the anode and Fe as the cathode.

In above eqn: $a_{Fe^{2+}}$ ↓

Also, with painting or Zn or Sn coating O_2 and H^+ cannot reach the surface and a_{O_2} & a_{H+} ↓

2. (10 marks)

(a) Provide definitions of the following terms in the context of acid-base equilibria:

(i) A Brønsted acid

A proton donor

(ii) A Brønsted base

A proton acceptor

(iii) A salt

The product of a reaction between an acid and a base

acid + base → salt (+ water)

(iv) A buffer solution

A solution that contains significant and comparable amounts of a weak acid-weak base conjugate pair. It can reduce the effect of added acid or base on the pH of the system

Question 2 continued on following page

Question 2 continued

(b) A chemist discovers a new, water-soluble compound, exoticaine. A 1.5×10^{-6} mol L^{-1} aqueous solution of exoticaine has a pH of 8.18. Circle, below, two words that best describe the acid-base properties of exoticaine:

pH > 7

STRONG WEAK ACID BASE

$pOH = -\log_{10} 1.5\times10^{-6} = 5.82$

$pH = 14 - pOH = 8.18$

3. (18 marks)

Formic acid (HCOOH) is an organic compound with $K_a = 1.8 \times 10^{-4}$.

(a) What is the pK_a of formic acid?

$pK_a = -\log_{10} K_a = 3.74$

(b) What is the pH of a 0.0100 mol L^{-1} solution of formic acid?

$HFor \rightleftharpoons H^+ + For^-$

$K_a = \frac{[H^+][For^-]}{[HFor]}$

$\approx \frac{[H^+]^2}{C_a}$ ← $K_a \gg K_w$, $K_a \ll 1$

$pH = -\log_{10}[H^+]$

$= 2.87$

$\Rightarrow [H^+] \approx \sqrt{K_a C_a}$

$= 0.00134\,2$ mol L^{-1}

(c) What is the pK_b of the formate anion ($HCOO^-$)?

$pK_a + pK_b = 14$

$pK_b = 14 - pK_a$

$= 14 - 3.74$

$= 10.26$

Question 3 continued on following page

Question 3 continued

(d) What is the pH of a 0.0050 mol L^{-1} solution of sodium formate (HCOONa)?

For Na

$For^- + H_2O \rightleftharpoons HFor + OH^-$

$K_b = \frac{[HFor][OH^-]}{[For^-]} \approx \frac{[OH^-]^2}{C_{salt}}$

$\Rightarrow [OH^-] \approx \sqrt{K_b C_{salt}}$

$K_b = 10^{-pK_b} = 10^{-10.26}$

$= 5.50 \times 10^{-11}$

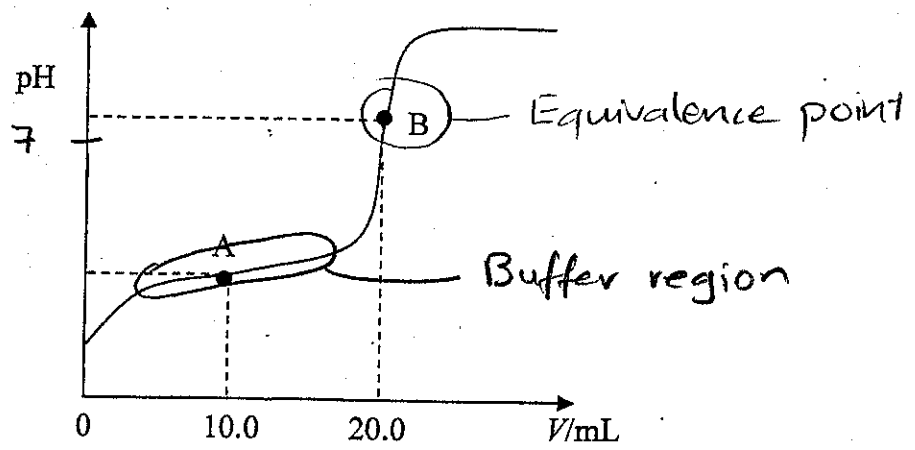
$= 5.24 \times 10^{-7}$

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

$= 6.28$

$pH = 14 - pOH = 7.72$

(e) The plot below was obtained from a titration involving 0.0100 mol L^{-1} solutions of formic acid and sodium hydroxide.



(i) Tick the box that correctly describes the titration:

Formic acid solution is being added to sodium hydroxide solution ☐

OR sodium hydroxide solution is being added to formic acid solution ☑

(ii) Indicate and clearly label the following on the above plot:

- The equivalence point
- The buffer region
- The approximate position of pH = 7 on the pH (y) axis

Question 3 continued on following page

Question 3 continued

(iii) Using your answers to earlier parts of this question, what is the pH corresponding to point A of the plot? ***Provide an explanation for your answer.***

$pH_{1/2eq} = pK_a = 3.74$ from (a)

(iv) Using your answers to earlier parts of this question, what is the pH corresponding to point B? ***Provide an explanation for your answer.***

At equivalence we have a salt solution with a concentration of $c_a/V_{total} = 0.005$ mol L^{-1}. So

$pH_{eq} = 7.72$ from (d)

(v) 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)
Bromophenol blue	3.8
Brilliant yellow	7.2
Thymolphthalein	10.0
2,4,6-Trinitrotoluene	12.3

We want an indicator with

$pK_a(\text{indicator}) \approx pH_{eq}$.

Best choice is brilliant yellow

4. (28 marks)

(a) For the combustion of ethane (1), use the thermodynamic data given below to calculate the following parameters at 298 K. (R = 8.314 J mol^{-1} K^{-1})

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad (1)$$

	ΔH_f° / kJ mol^{-1}	ΔG_f° / kJ mol^{-1}	S°/J K^{-1} mol^{-1}
$C_2H_6(g)$	-84.7	-32.8	unknown
$O_2(g)$	0	0	+205.1
$CO_2(g)$	-393.5	-394.4	+213.7
$H_2O(l)$	-285.8	-237.2	+69.9

(i) ΔH°

$$\Delta H^\circ = 2.\Delta H_f^\circ(CO_2) + 3.\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_2H_6)$$
$$= 2(-393.5) + 3(-285.8) - (-84.7)$$
$$= -1,559.7 \text{ kJ mol}^{-1}$$

(3 mark)

(ii) ΔG°

$$\Delta G^\circ = 2.\Delta G_f^\circ(CO_2) + 3.\Delta G_f^\circ(H_2O) - \Delta G_f^\circ(C_2H_6)$$
$$= 2(-394.4) + 3(-237.2) - (-32.8)$$
$$= -1,467.6 \text{ kJ mol}^{-1}$$

(3)

(iii) ΔS°

$$\Delta G^\circ = \Delta H^\circ - T.\Delta S^\circ$$
$$\therefore \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$
$$= \frac{[-1559.7 - (-1467.6)] \times 1000}{298} \qquad \left(\frac{kJ}{mol} \times \frac{J}{kJ} \times \frac{1}{K}\right)$$
$$= \frac{-92.1 \times 1000}{298} = -309.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

(3)

Question 4 continued on following page

Question 4 continued

(iv) S° for ethane ($C_2H_6(g)$)

$$\Delta S^\circ = 2\times S^\circ(CO_2) + 3\times S^\circ(H_2O) - S^\circ(C_2H_6) - \tfrac{7}{2}\times S^\circ(O_2)$$

$$\therefore\ S^\circ(C_2H_6) = 2\times S^\circ(CO_2) + 3\times S^\circ(H_2O) - \tfrac{7}{2}\times S^\circ(O_2) - \Delta S^\circ$$

$$= 2\times 213.7 + 3\times 69.9 - \tfrac{7}{2}\times 205.1 - (-309.1)$$

$$= +228.4\ \ J\,K^{-1}\,mol^{-1}$$

(4 marks)

(v) K (the thermodynamic equilibrium constant) at 298 K

$$\Delta G^\circ = -RT\ln_e K$$

$$\therefore\ K = \exp(-\Delta G^\circ/RT)$$

$$= \exp\left\{\frac{+1467.6\times 1000}{8.314\times 298}\right\}$$

$$= \exp(592.35) \qquad (= 1.8\times 10^{257})$$

← Full marks to here ("calculator overflow") (4)

(vi) K at 400 K (assume that ΔH° and ΔS° are constant between 298 and 400 K)

$$\ln_e\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\} \qquad (T_1 = 298K,\ T_2 = 400K)$$

$$\therefore\ \ln_e\left(\frac{K_{400}}{K_{298}}\right) = \frac{-1559.7\times 1000}{8.314}\left\{\frac{1}{298} - \frac{1}{400}\right\}$$

$$= -160.53$$

$$\therefore\ K_{400}/K_{298} = \exp(-160.53) = 1.92\times 10^{-70}$$

$$K_{400} = 1.92\times 10^{-70}\times K_{298} \qquad (= 3.44\times 10^{187})$$

(4)

↑ Full marks to here ("calculator overflow")

Question 4 continued on following page

Question 4 continued

(b) By considering the phase and number of moles of each reaction component in reaction (1), comment on the sign you have obtained for ΔS°.

Reactants comprise $1 + \frac{7}{2} = 4.5$ moles of gas
Products " 2 moles of gas + 3 moles of liquid
∴ Lower total entropy expected as reaction proceeds because liquid phase is more ordered (than gas).
∴ ΔS° expected to be NEGATIVE (2 marks)

(c) Calculate the changes of entropy of the surroundings (ΔS°_{surr}) and of the universe (ΔS°_{univ}) induced by reaction (1) under standard thermodynamic conditions.

$$\Delta S^\circ_{surr} = \frac{\Delta H^\circ_{surr}}{T} = -\frac{\Delta H^\circ_{system}}{T} \quad (1^{st}\ Law)$$

$$= +\frac{1559.7 \times 1000}{298}$$

$$= +5233.8 \ J\,K^{-1}\,mol^{-1}$$

$$\Delta S^\circ_{universe} = \Delta S^\circ_{system} + \Delta S^\circ_{surr}$$

$$= -309.1 + 5233.8 = +4925 \ (J\,K^{-1}\,mol^{-1})$$

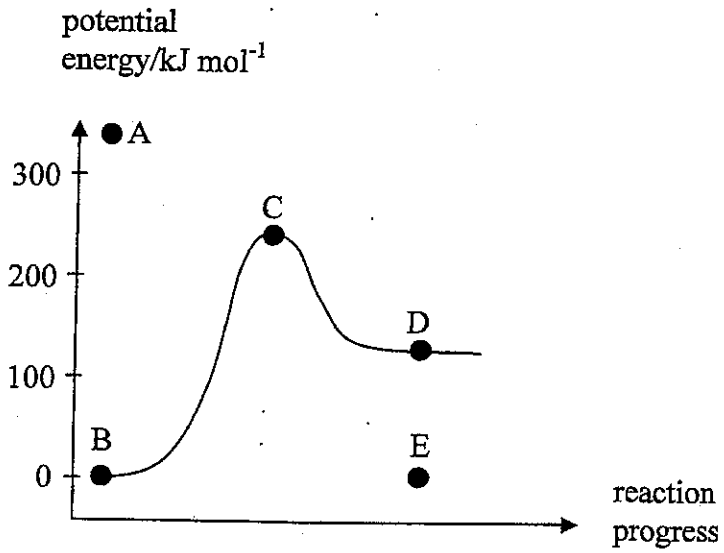
(3)

(d) Comment on the direction of spontaneous change for reaction (1) under standard thermodynamic conditions.

Under standard conditions: $\Delta G = \Delta G^\circ = -1467.6$ $(kJ\ mol^{-1})$
This is a large NEGATIVE quantity
Therefore under standard conditions (all gas pressures at 1 atm + pure liquid H_2O) the reaction will proceed spontaneously in the FORWARD direction (2)

5. (14 marks)

A reaction has an energy profile given by the figure below.



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

Elementary as the reaction proceeds via a single transition state (= "activated complex" or "energy barrier"). (A complex reaction would have two (or more) transition states.)

(2 marks)

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

Endothermic as energy of products is higher than the energy of reactants.

(∴ ΔU or ΔH are both positive)

(2)

Question 5 continued on following page

Question 5 continued

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

(i) reactants [B]

(ii) products [D]

(iii) transition state [C]

(3 marks)

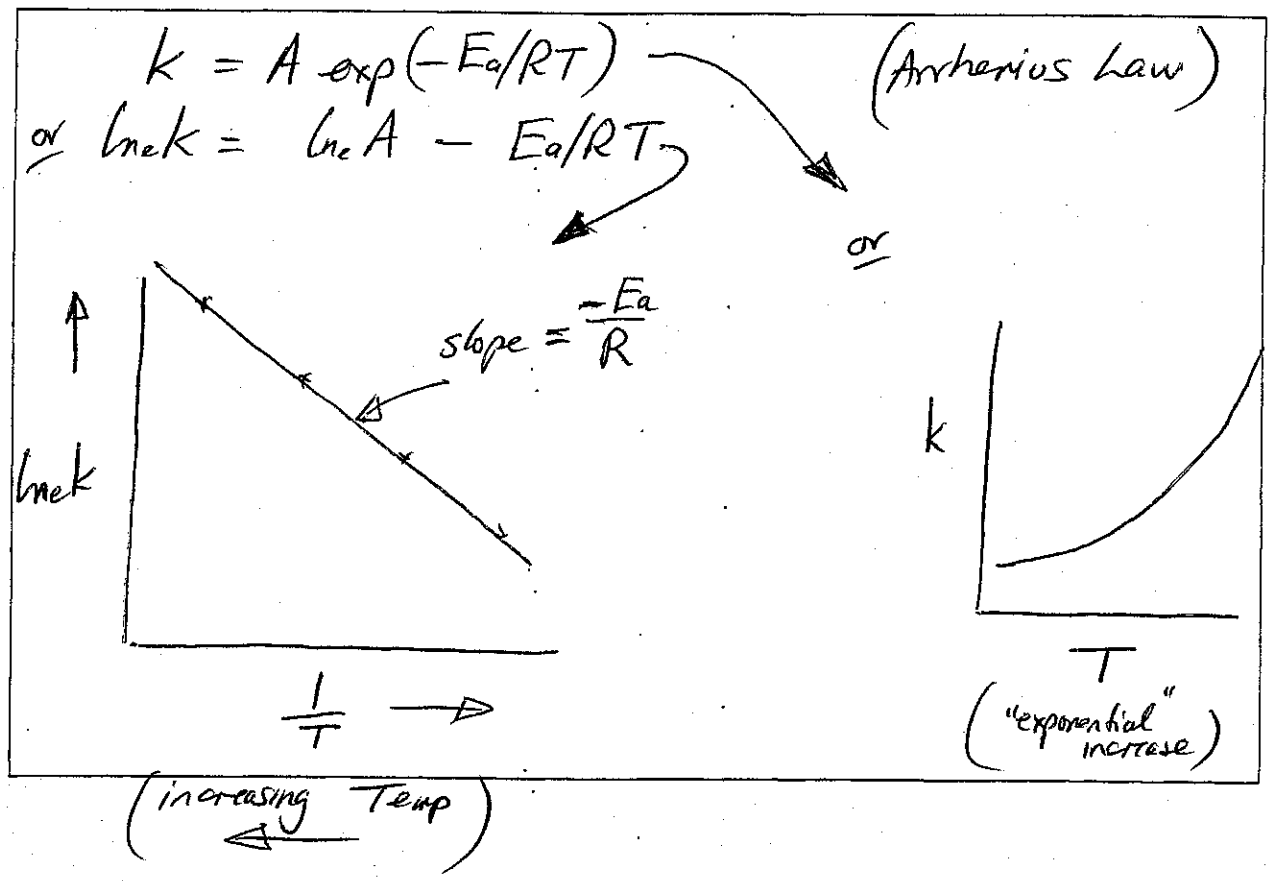
(d) Estimate the values (including units) of the following parameters (no significant calculations required).

(i) $\Delta H°_{reaction}$ [+120 (±20)] kJ mol^{-1}

(ii) E_a [+240 (±20)] " "

(4)

(e) In what way would you predict the rate constant for the reaction to be altered by an increase in the temperature of the system? Explain your reasoning, sketching a figure if you wish.



(3)

6. (10 marks)

Three experiments were undertaken at constant temperature to determine the rate law for the reaction

$$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(aq)$$

The results were:

Experiment #	$[H_2PO_4^-]_0$/mol L^{-1}	$[OH^-]_0$/mol L^{-1}	Initial Rate / mol L^{-1} s^{-1}
1	0.0030	0.00080	0.0080
2	0.0030	0.00040	0.0021
3	0.0090	0.00040	0.0062

Assume Rate $= k[H_2PO_4^-]^\alpha [OH^-]^\beta$

(a) Determine the orders of the reaction with respect to $H_2PO_4^-$ and OH^-.

Expt 3 vs Expt 2 $\Rightarrow$ $\frac{IR(3)}{IR(2)} = \frac{0.0062}{0.0021} = \frac{k(0.009)^\alpha (0.0004)^\beta}{k(0.003)^\alpha (0.0004)^\beta}$

$= 2.95 = 3^\alpha$

$\therefore \alpha = 1$ (order w.r.t. $H_2PO_4^-$) (3)

Similarly

Expt 1 vs Expt 2 $\Rightarrow$ $\frac{IR(1)}{IR(2)} = \frac{0.0080}{0.0021} = \left(\frac{0.00080}{0.00040}\right)^\beta$

$= 3.81 = 2^\beta$

$\therefore \beta = 2$ (order w.r.t. OH^-) (3)

(b) What is the **overall** order of the reaction?

Overall order $= \alpha + \beta = 2 + 1 = 3$ (1)

(c) Calculate the rate constant for this reaction. What are the units of the rate constant?

Take Expt (1): Initial Rate $= k[H_2PO_4^-][OH^-]^2$

$\therefore k = \frac{0.0080}{0.0030 \times (0.00080)^2}$

$= 4.17 \times 10^6$ $L^2 mol^{-2} s^{-1}$ (3)

7. (18 marks)

(a) Use the data below (for reactions 2 and 3) to calculate the equilibrium constant (K_1) for reaction 1 at 298 K:

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

---

2. $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ $\quad K_2 = 1.74 \times 10^6$

3. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K_3 = 2.32 \times 10^{12}$

Reaction (2) × 2 is: $2SO_2 + 2NO_2 \rightleftharpoons 2SO_3 + 2NO$

Reaction (3) is: $2NO + O_2 \rightleftharpoons 2NO_2$

Adding gives: $2SO_2 + O_2 \rightleftharpoons 2SO_3$

That is Reaction (1) $\equiv$ 2 × Reaction (2) + Reaction (3)

$\therefore \quad K_1 = K_2^2 K_3$

$= (1.74 \times 10^6)^2 \times 2.32 \times 10^{12}$

$= 7.02 \times 10^{24}$

(8 marks)

Question 7 continued on following page

Question 7 continued

(b) Consider the case where reactions 2 and 3 represent a two-step mechanism for reaction 1.

(i) Which of the reaction components (products or reactants) in reactions 2 and 3 would be the catalyst?

NO_2 (1)

(ii) Which of the reaction components in reactions 2 and 3 would be an intermediate?

NO (1)

(c) Provide a short definition of Le Chatelier's principle.

When a "stress" or "perturbation" is applied to a system at equilibrium (through addition of material; change of volume (or total pressure); or temperature change) the equilibrium position of the system shifts so as to minimise the effect of the stress/perturbation. (3)

Question 7 continued on following page

Question 7 continued

(d) Each of the following cases, (i) to (iv), represents a *change* (stress) that may be applied to a system at equilibrium. You should use one of the following **letters** (A, B, C or D) to indicate how the (equilibrium) system for **reaction 1** responds to the change:

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

[A] Net shift in the direction of the forward reaction

[B] No net change

[C] Net 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) $SO_2(g)$ is added at constant volume and temperature

System response: A Additional information:

(ii) Volume is increased at constant temperature

System response: C Additional information:

(iii) $N_2(g)$ is added at constant volume and temperature

System response: B Additional information:

(iv) Temperature is increased at constant pressure

System response: D Additional information: Sign of ΔH° for reaction

(5)

END OF PAPER