FAMILY NAME: ....
GIVEN NAME: ....
STUDENT ID: ....
SIGNATURE: ....

University of Canterbury

End-of-year Examinations 2010

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

Time Allowed: 2.5 HOURS

Number of pages: 17 pages
2 pages (formulae and periodic table)

Answer **ALL** questions

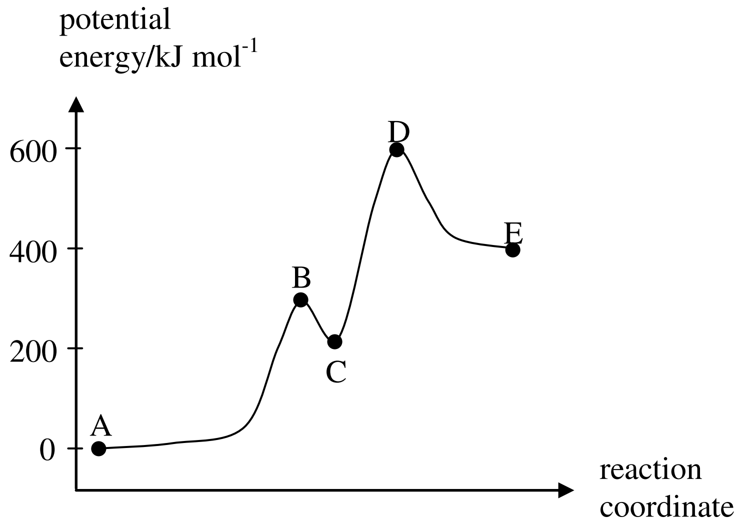
Total marks = 120

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

For examiners use only

1-3	4,5	6	7	8,9	Total
/30	/18	/30	/22	/20	/120

1. (8 marks)



Using the figure above, which refers to the progress of a chemical reaction, answer the following:

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

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

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

(i)	reactants	
(ii)	products	
(iii)	intermediates	
(iv)	transition states	

2. (12 marks)

The rate data in the following table were obtained at 80°C for the reaction in aqueous solution

$$A + B \rightarrow C + D$$

Expt	Initial concentration (mol L^{-1})		Initial rate
	$[A]_0$	$[B]_0$	(mol L^{-1} s^{-1})
1	0.0100	0.0250	3.6×10^{-4}
2	0.0050	0.0250	1.8×10^{-4}
3	0.0100	0.0125	0.9×10^{-4}

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

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

(i) the order of reaction with respect to A;

(ii) the order of reaction with respect to B;

(iii) the overall order of reaction.

(c) From your answers in (b) and the data in the table, determine the value of the rate constant at 80°C, specifying its units.

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

3. (10 marks)

$N_2O_4(g)$ is unstable at room temperature and decomposes according to reaction (1):

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad (1)$$

(a) Assuming first-order kinetics, give a mathematical expression for the ***differential rate law*** for reaction (1).

(b) Define, ***in words***, what is meant by the half-life of a first-order reaction.

(c) Give a mathematical expression for the ***integrated rate law*** for reaction (1) and use it to show that the half life ($t_{1/2}$) of a first-order reaction can be mathematically defined by equation (2):

$$t_{1/2} = (1/k)\log_e(2) \qquad (2)$$

(d) At a temperature of 273 K, reaction (1) has a rate constant of $4.8 \times 10^3\ \mathrm{s}^{-1}$. In a particular experiment, $N_2O_4(g)$ at 273 K has an initial partial pressure of 0.80 bar. Calculate the partial pressure of $N_2O_4(g)$ after 100 μs (1×10^{-4} s)?

(e) The rate constant for reaction (1) is 1.07×10^{4} s^{-1} at 283 K. Calculate the activation energy. ($R = 8.314$ J mol^{-1} K^{-1})

4. (4 marks)

At 1000 K the following reactions have the equilibrium constants shown:

$$2CH_4(g) + O_2(g) \rightleftharpoons 2CO(g) + 4H_2(g) \qquad K_1 = 4.0 \times 10^{22} \qquad (1)$$

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_2 = 0.73 \qquad (2)$$

Calculate K_3, the equilibrium constant for reaction (3) at 1000 K:

$$CH_4(g) + H_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g) + 3H_2(g) \qquad (3)$$

5. (14 marks)

Consider the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(a) Write expressions for the thermodynamic equilibrium constant, K, in terms of:

(i) the activities of the reaction components;

(ii) the partial pressures of the reaction components.

(b) What are the units of a thermodynamic equilibrium constant? ***Explain your answer.***

(c) A container is filled to a pressure of 1 bar with pure $PCl_5(g)$. After the system has reached equilibrium at 250 °C, the partial pressure of Cl_2 is found to be 0.66 bar.

(i) What is the partial pressure of PCl_3?

(ii) What is the partial pressure of PCl_5?

(iii) What is *K* for the reaction at 250 °C?

(d) Each of the following cases, (i) to (iii), represents a *change* (stress) that may be applied to a system that is initially at equilibrium. You should use one of the following **letters** (A, B, C or D) to indicate how the (equilibrium) system for the reaction you have been considering, i.e.:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

responds to the change.

[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) $Cl_2(g)$ is added at constant volume and temperature

System response: ☐ Additional information: ☐

(ii) Volume is increased at constant temperature

System response: ☐ Additional information: ☐

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

System response: ☐ Additional information: ☐

6. (30 marks)

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

$$4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l) \qquad (1)$$

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$\Delta G_f^\ominus$ / kJ mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}
$HCl(g)$	-92.31	-95.30	unknown
$O_2(g)$	0	0	+205.1
$Cl_2(g)$	0	0	+223.1
$H_2O(l)$	-285.83	-237.13	+69.9

(i) $\Delta H^\ominus$

(ii) $\Delta G^\ominus$

(iii) $\Delta S^\ominus$

(iv) $S^\ominus$ for $HCl(g)$

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

(vi) K at 400 K (assume that $\Delta H^\ominus$ and $\Delta S^\ominus$ are constant between 298 and 400 K)

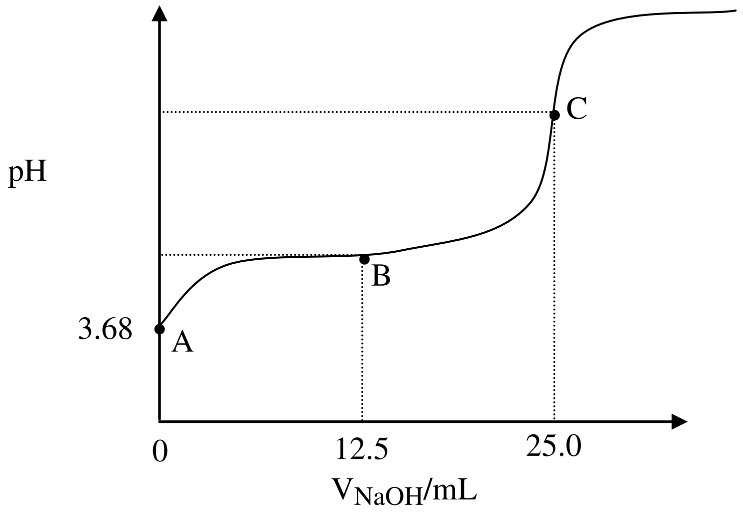
(b) Why do $O_2(g)$ and $Cl_2(g)$ have $S^\ominus$ values which are **not** equal to zero (as are their respective values for $\Delta H_f^\ominus$ and $\Delta G_f^\ominus$)?

(c) By considering the phase and number of moles of each reaction component in reaction (1), comment on the sign you have obtained for $\Delta S^\ominus$.

(d) Calculate the changes of entropy of the surroundings ($\Delta S^{\ominus}_{\text{surr}}$) and of the universe ($\Delta S^{\ominus}_{\text{univ}}$) induced by reaction (1) under standard thermodynamic conditions.

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

7. (22 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 20.0 mL sample of a solution of weak acid, HA, of concentration 0.125 mol L^{-1} is titrated with NaOH solution. The NaOH solution has unknown concentration, C_{NaOH}, and V_{NaOH} represents the volume in mL of NaOH which has been added. [Data: $K_w = 1.00 \times 10^{-14}$.]

(a) **On the figure above** clearly indicate and label the following:

(i) the equivalence point
(ii) a buffer region

(b) Calculate C_{NaOH}.

(c) Using the initial pH value for the solution (3.68), calculate K_a (the acid dissociation constant) for HA.

(d) What is the pH at point B?

(e) Prove the general result that K_b (base ionisation constant for the base X^-, ie conjugate base of the acid, HX) is given by $K_b(X^-) = K_w/K_a(HX)$.

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

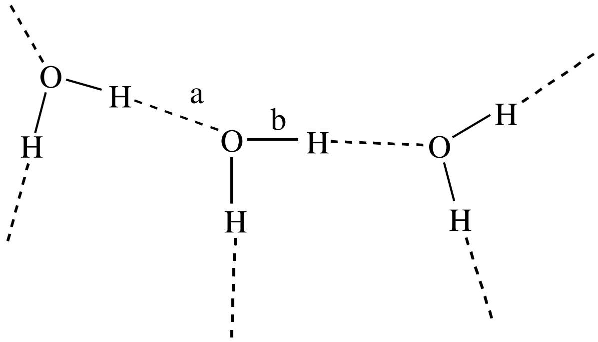
(g) The end-point of this titration could be detected using an indicator. Of the indicators listed below, which would be the most suitable? Explain the reason for your answer.

Indicator	**pK_a (indicator)**
Bromophenol blue	3.8
Bromophenol blue	6.8
Phenolphthalein	9.1
Alizarin yellow R	11.1

(h) State clearly what you understand the terms “end-point” and “equivalence point” to mean.

8. (15 marks)

(a) The diagram represents some interacting molecules in a sample of liquid water.



Choose the letter (a or b) that shows:

(i) an intermolecular bond ______________

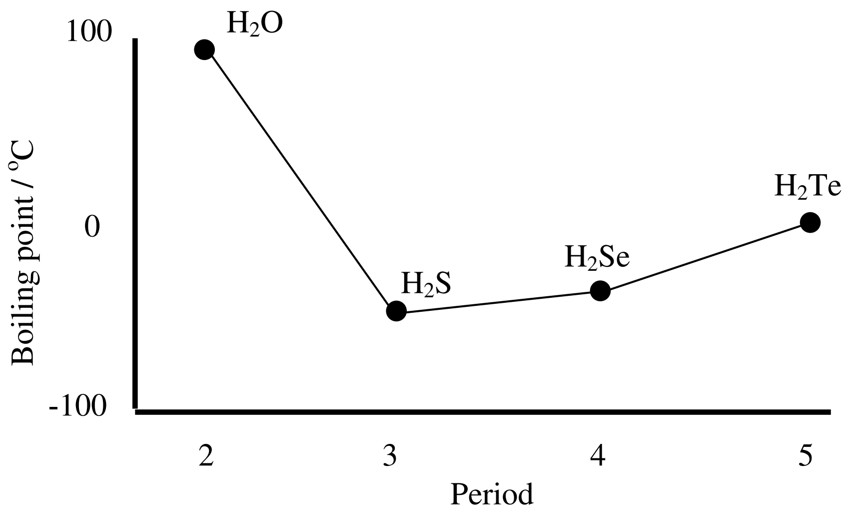
(ii) a hydrogen bond ______________

(iii) a covalent bond ______________

(iv) a bond which is broken during boiling ______________

(b) Explain, using diagrams if necessary, why ice is less dense than water.

(c)



(i) Explain why water has the highest boiling point of the compounds in the diagram above.

(ii) Why do the boiling points increase from H_2S through to H_2Te?

9. (5 marks)

In the production of biodiesel from canola oil, glycerol is formed. Glycerol can potentially damage car engines. When a known excess of periodic acid (HIO_4) is added to an unknown amount of glycerol, the quantity of glycerol in the sample can be calculated by determining the molar excess of periodate ions (IO_4^-) remaining after the reaction. This is determined by reacting the excess periodiate with excess iodide (equation **1**).

$$IO_4^-(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + IO_3^-(aq) + H_2O(l) \qquad \textbf{1}$$

The amount of triodide (I_3^-) is easily determined by titration with thiosulfate solution (equation **2**).

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq) \qquad \textbf{2}$$

(a) Write the balanced equation for the overall redox reaction using equations **1** and **2.**

After several 25 mL solutions, each prepared from 5 g samples of biodiesel, were analysed the average number of moles of glycerol per sample was found to be 5.37×10^{-5} mol.

(b) What is the average mass of glycerol in the biodiesel samples? (M_R glycerol $= 92$ g mol^{-1})

(c) Calculate the average wt% of glycerol in the samples.

(d) Is this within the US and European of guidelines of a maximum of 0.25 wt%?

END OF PAPER

(Physical Chemistry Formulae and Periodic Table follow)

Physical Chemistry Formulae

$PV = nRT$

$P_A = x_A P_{total}$ where $P_{total} = \sum_i P_i$ and $x_A = \frac{n_A}{\sum_i n_i}$

$\Delta U = q + w$ $w_P = -P\Delta V$

$H = U + PV$ $\Delta H = \Delta U + RT\Delta n_{gas}$ when $\Delta T = 0$

$q = ms\Delta T$

For calorimetry $\Delta H = -C_P\Delta T$ $\Delta U = -C_V\Delta T$ *where* C_P *and* $C_V = ms$

$\Delta H_{reaction} = \sum_{prods} \nu_{prod}\Delta_f H(\text{prod}) - \sum_{reacts} \nu_{react}\Delta_f H(\text{react})$

$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$

For $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$, Rate $= \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

For: Rate $= \frac{-d[A]}{dt} = k$ $[A] = [A]_0 - kt$

For: Rate $= \frac{-d[A]}{dt} = k[A]$ $[A] = [A]_0 e^{-kt}$ and $t_{1/2} = (1/k)\log_e(2)$

$k = Ae^{-E_a/RT}$ $\log_e\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\Delta S = \sum_{prods} \nu_{prod}S(\text{prod}) - \sum_{reacts} \nu_{react}S(\text{react})$ $\Delta S_{phase\ change} = \frac{\Delta H_{phase\ change}}{T_{critical}}$

$\Delta G = \Delta H - T\Delta S$ $\Delta G = \sum_{prods} \nu_{prod}\Delta_f G(\text{prod}) - \sum_{reacts} \nu_{react}\Delta_f G(\text{react})$

$\Delta G = \Delta G^{\ominus} + RT\log_e Q$ $\Delta G^{\ominus} = -RT\log_e K$

$\log_e K = \frac{-\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}$ $\log_e\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$K_a = \frac{[H^+][A^-]}{[HA]}$ $K_b = \frac{[BH^+][OH^-]}{[B]}$

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

$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) = \text{p}K_a + \log_{10}\left(\frac{n(A^-)}{n(HA)}\right)$

1 Pa = 1 N m^{-2} = 1 J m^{-3}; 1 J = 1 N m;
1 atm = 760 torr = 1.013×10^5 Pa = 101.3 kPa = 1013 mbar
$N_A = 6.022 \times 10^{23}$ mol^{-1}
$R = 8.314$ J mol^{-1} K^{-1} = 0.08205 L atm mol^{-1} K^{-1}
0°C = 273.15 K

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)