

FULL NAME: .....

STUDENT ID: .....

SIGNATURE: .....

University of Canterbury

## Mid Year Examination and Test Period 2008

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

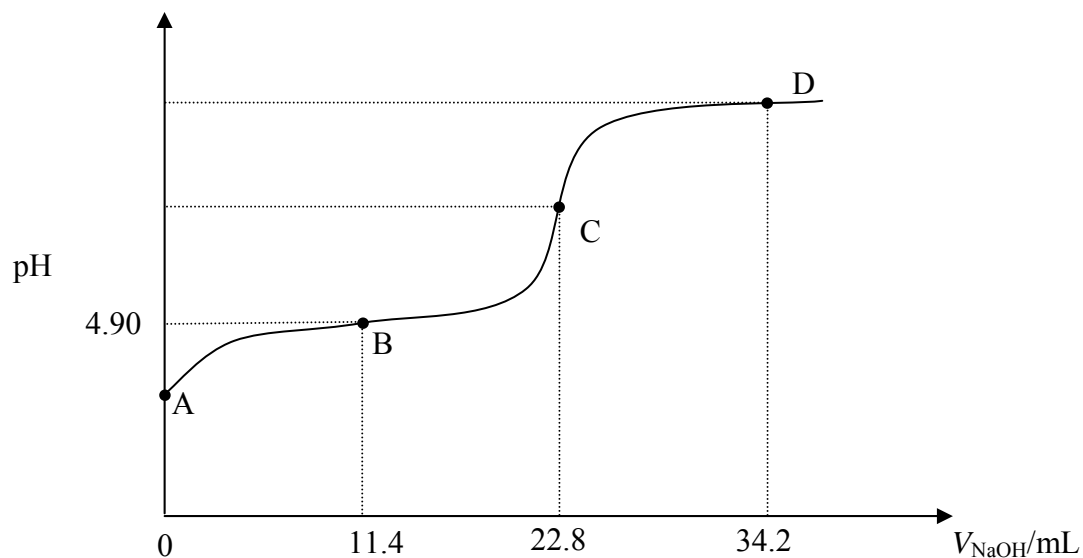
NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

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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?

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

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

(i) the equivalence point;

(ii) a buffer region.

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

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

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

- (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

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

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

- (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

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

2. (10 marks)

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

(i) system;

(ii) state function;

(iii) enthalpy;

(iv) second law of thermodynamics;

(v) third law of thermodynamics.

3. (14 marks)

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



substance	$\Delta H^\circ_f$ (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)

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

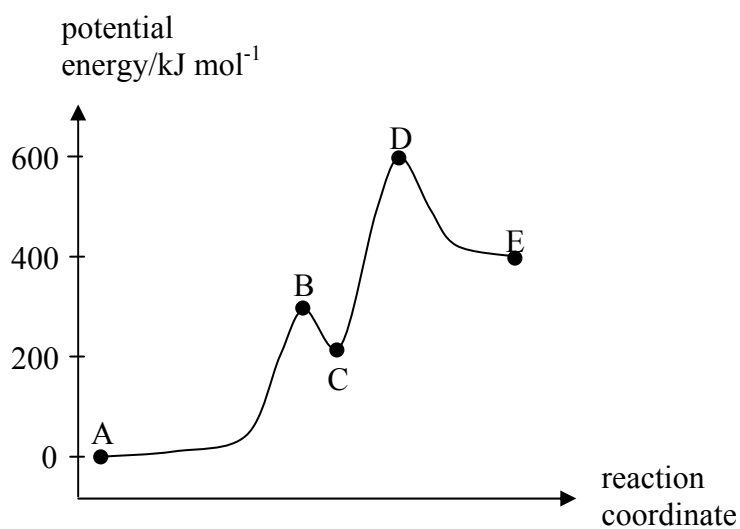
(c) From your answers in (a) and (b), calculate  $\Delta S^\circ$  for reaction (1). (If you were unable to obtain answers, use the **incorrect** values  $\Delta H^\circ = 10.3 \text{ kJ mol}^{-1}$  and  $\Delta G^\circ = 5.0 \text{ kJ mol}^{-1}$ .)

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

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

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

4. (8 marks)



Using the figure above, answer the following:

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

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

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

(i) reactants

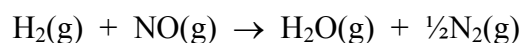
(ii) products

(iii) intermediates

(iv) transition states

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.

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

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

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

(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 700°C, specifying its units.

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

6. (18 marks)

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

<b>Reduction Half-reaction</b>	<b><math>E^\circ / \text{V}</math></b>
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+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?

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

- (iii) Which of the ions in the table will  $\text{Zn}(\text{s})$  reduce?

- (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.

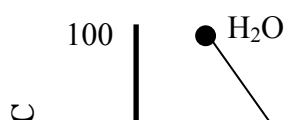
- (v) Calculate the equilibrium constant for the reaction of  $\text{Zn}(\text{s})$  with  $\text{Cu}^{2+}(\text{aq})$ .

$$[R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.]$$

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

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

7. (4 marks)



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

- (ii) Explain why the boiling points increase from  $\text{H}_2\text{S}$  to  $\text{H}_2\text{Te}$ .

8. (1 mark)

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

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

winter

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

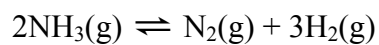
Vapour Pressure

Surface Tension

Density of ice

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;

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

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

(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  $P_{\text{NH}_3} = 1.00$  atm and  $P_{\text{H}_2} = 0.1$  atm. What is the equilibrium partial pressure of  $\text{N}_2(\text{g})$ ?

(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:

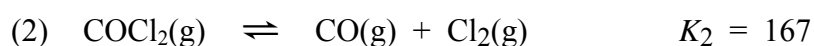
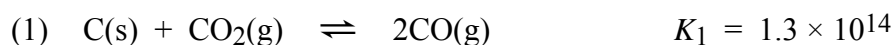
Additional information:

13. (10 marks)

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

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

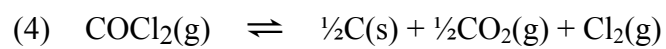
- (c) At 1123 K the following reactions have the equilibrium constants shown:



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



- (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.



**END OF PAPER**

## Physical Chemistry Formulae

$$PV = nRT$$

$$P_A = x_A P_{\text{total}}$$

$$\text{where } P_{\text{total}} = P_A + P_B \quad \text{and} \quad x_i = \frac{n_i}{\sum_i n_i}$$

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

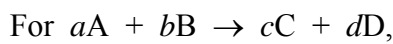
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

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

$$C_P = dH/dT \quad (\text{when } \Delta P = 0)$$

$$C_V = dU/dT \quad (\text{when } \Delta V = 0)$$

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



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

$$\text{For Rate} = \frac{-d[A]}{dt} = k,$$

$$[A] = [A]_0 - kt$$

$$\text{For Rate} = \frac{-d[A]}{dt} = k[A],$$

$$[A] = [A]_0 e^{-kt} \quad \text{and} \quad t_{1/2} = (1/k) \log_e(2)$$

$$k = A e^{-E_a/RT}$$

$$\log_e \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

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

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

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

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T_{\text{critical}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \sum_{\text{prods}} \nu_{\text{prod}} \Delta G_f(\text{prod}) - \sum_{\text{reacts}} \nu_{\text{react}} \Delta G_f(\text{react})$$

$$\Delta G = \Delta G^\circ + RT \log_e Q$$

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

$$\log_e K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\log_e \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$w_{\text{elect}} = \Delta G = -nFE$$

$$\Delta G^\circ = -RT \log_e K = -nFE^\circ$$

$$E^\circ = \frac{RT}{nF} \log_e K = \frac{2.303RT}{nF} \log_{10} K$$

$$\text{At } 25^\circ\text{C: } E^\circ = \frac{0.0591 \text{ V}}{n} \log_{10} K$$

$$E = E^\circ - \frac{RT}{nF} \log_e Q = E^\circ - \frac{2.303RT}{nF} \log_{10} Q$$

$$\text{At } 25^\circ\text{C: } E = E^\circ - \frac{0.0591 \text{ V}}{n} \log_{10} Q$$

$R$  Gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup> or 0.082 L atm mol<sup>-1</sup> K<sup>-1</sup>)

$F$  Faraday Constant (96489 C mol<sup>-1</sup>)

## 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
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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)
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