

FULL NAME: .....

STUDENT ID: .....

SIGNATURE: .....

University of Canterbury

## Mid Year Examination and Test Period 2009

Prescription Number(s): CHEM 111

Paper Title: General Chemistry A

Time Allowed: 2.5 HOURS

Number of pages: 18 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.

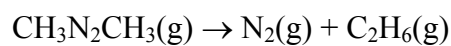
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For examiners use only

1,2	3,4	5	6,7	8-12	13,14	Total/120

1. (13 marks)

Azomethane decomposes as follows:



At 305 °C this occurs with a rate constant of  $k = 0.2310 \text{ min}^{-1}$ .

- (a) The reaction is first-order. How could you have deduced this from the information above?

- (b) For an experiment at 305 °C, the partial pressure of azomethane is initially 317.5 mm Hg.

Calculate the following after 120 s:

- (i) The partial pressure of azomethane

- (ii) The change in the pressure of  $\text{N}_2(\text{g})$

(iii) The change in the total pressure

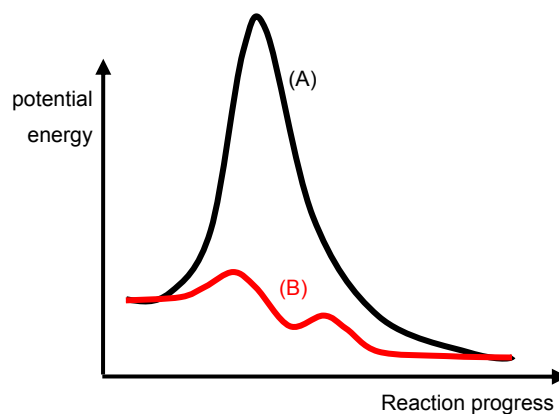
(c) How long would it take for half of the azomethane to have decomposed?

(d) At 325 °C the rate constant is found to have increased to  $k = 0.5323 \text{ min}^{-1}$ . What is the activation energy for the reaction?

[ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $0 \text{ }^\circ\text{C} = 273.15 \text{ K}$ ]

2. (7 marks)

The diagram below relates to two possible pathways for a reaction.



(a) Is pathway (A) that of an *elementary* or *complex* reaction? Explain your answer.

(b) Is pathway (B) that of an *elementary* or *complex* reaction? Explain your answer.

(c) Which of (A) or (B) represents the pathway of a *catalyzed* reaction? Explain your answer.

(d) Indicate the location of a *transition state* on the above diagram.

3. (14 marks)

Nitrous acid ( $\text{HNO}_2$ ) is a weak acid with  $K_a = 4.5 \times 10^{-4}$ . [ $K_w = 1.00 \times 10^{-14}$ .]

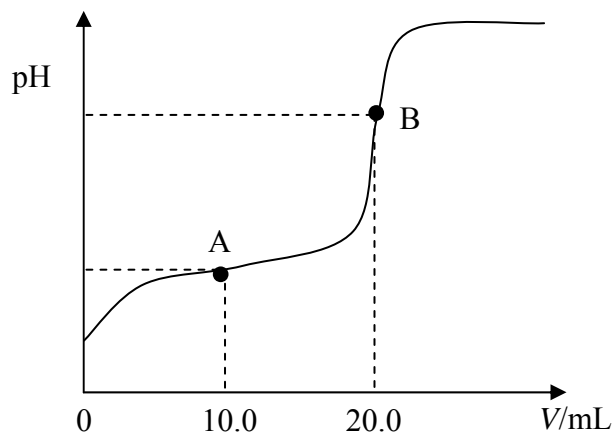
(a) What is the  $\text{p}K_a$  of nitrous acid?

(b) What is the pH of a  $0.0500 \text{ mol L}^{-1}$  solution of nitrous acid?

(c) What is the  $\text{p}K_b$  of the nitrite anion ( $\text{NO}_2^-$ )?

(d) What is the pH of a  $0.0250 \text{ mol L}^{-1}$  solution of sodium nitrite ( $\text{NaNO}_2$ )?

- (e) The plot below was obtained from a titration involving  $0.0500 \text{ mol L}^{-1}$  solutions of nitrous acid and sodium hydroxide.



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

Nitrous acid solution is being added to sodium hydroxide solution

**OR** sodium hydroxide solution is being added to nitrous acid solution

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

- The equivalence point
- The buffer region

- (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.*

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

4. (10 marks)

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

(i) A Brønsted acid

(ii) A Brønsted base

(iii) A salt

(iv) A buffer solution

(b) A  $0.10 \text{ mol L}^{-1}$  solution of caffeine has a pH of 11.8. Circle, below, two words that best describe the acid-base properties of caffeine:

STRONG

WEAK

ACID

BASE

5. (12 marks)

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

(i) first law of thermodynamics;

(ii) entropy;

(iii) surroundings;

(iv) spontaneity;

(v) equilibrium.

(b) Give the names of the functions  $G$ ,  $T$  and  $Q$  in the equation:

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

6. (12 marks)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{H}_2\text{S}(\text{g})$	-20.6	205.8
$\text{O}_2(\text{g})$	0	205.1
$\text{SO}_2(\text{g})$	-296.8	248.2
$\text{H}_2\text{O}(\text{g})$	-241.8	188.8

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

(a) For the reaction:  $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$   
use the thermodynamic data above to calculate the following:

(i) The standard molar enthalpy change,  $\Delta H^\circ$ ;

(ii) The standard molar entropy change,  $\Delta S^\circ$ ;

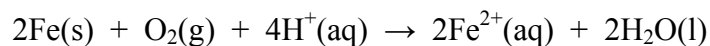
(iii)  $\Delta G^\circ$  for the reaction at  $25^\circ\text{C}$ ;

(iv) The equilibrium constant,  $K$ , for the reaction at  $25^\circ\text{C}$ .

(b) For the reaction in (a) predict, with an explanation of your reasoning, whether  $K$  would *increase*, *decrease*, or *remain unchanged* when the temperature is raised to  $100^\circ\text{C}$ .

7. (18 marks)

The corrosion of iron in seawater in an aerobic environment may be represented by the following overall equation:



(a) Write down the half-cell reaction for the oxidation process.

(b) Write down the half-cell reaction for the reduction process

(c) Draw a conventional cell diagram for the overall reaction. On the diagram, clearly indicate the *anode*, the *cathode* and the *positive electrode*.

(d) Calculate the standard voltage of the cell,  $E^\circ_{\text{cell}}$ , given the following standard reduction potentials:

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}; \quad E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}; \quad E^\circ_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}} = +1.23 \text{ V}.$$

- (e) Calculate the voltage generated in a 'corrosion cell' when a piece of metallic iron dips into seawater with  $[\text{Fe}^{2+}] = 2 \times 10^{-3} \text{ mol L}^{-1}$  at  $\text{pH} = 5.5$ , and is at the same time in contact with air at 1 atm. Assume that the mole fraction of  $\text{O}_2$  in air is 0.2 and that  $T = 298 \text{ K}$ . [ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ]

- (f) Describe two ways by which the above corrosion process might be prevented.

8. (3 marks)

The hydrogen bond energy for water is  $25 \text{ kJ mol}^{-1}$ . What is a hydrogen bond (why is it formed)?

9. (2 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

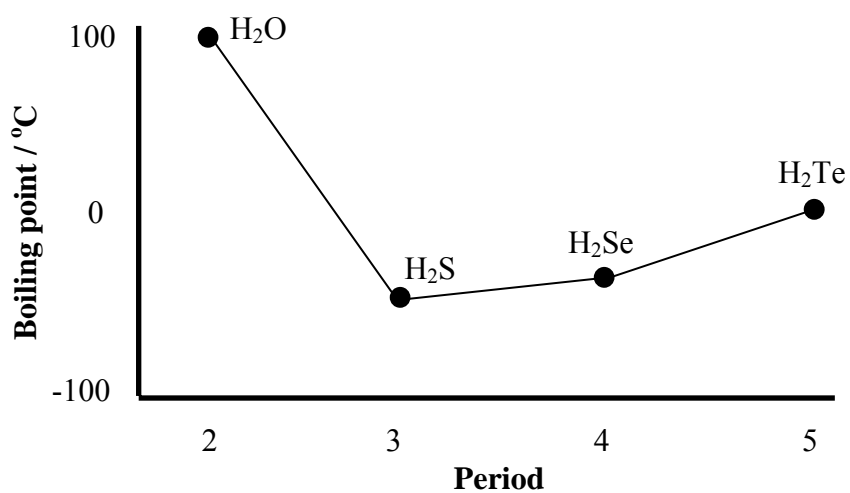
10. (4 marks)

- (a) The mobility of alkali metal cations in aqueous solution under the influence of an electric field **increases** with **increasing** ion size, i.e.,  $\text{Cs}^+$  is more mobile than  $\text{Li}^+$ . Explain.

- (b) Despite the trend in (a), the  $\text{H}_3\text{O}^+$  ( $\text{H}^+$ ) ion in aqueous solution exhibits a much higher mobility than expected. Use a sketch to illustrate the mechanism responsible for this apparent anomaly.

11. (4 marks)

Using the plot below



(a) Explain why the boiling points increase from H<sub>2</sub>S to H<sub>2</sub>Te?

(b) Explain why the boiling point for water appears to deviate so drastically from the trend evident in going from H<sub>2</sub>Te to H<sub>2</sub>Se to H<sub>2</sub>S.

12. (3 marks)

Complete the Table below to qualitatively indicate the solubility of the salts made up from the cations and anions given. Use **1** for soluble, **2** for sparingly soluble and **3** for insoluble.

<b>solubility</b>	<b>Mg<sup>2+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>Ba<sup>2+</sup></b>
<b>OH<sup>-</sup></b>			
<b>CO<sub>3</sub><sup>2-</sup></b>			
<b>SO<sub>4</sub><sup>2-</sup></b>			

13. (9 marks)

(a) Explain the difference between *static equilibria* and *dynamic equilibria*.

(b) Are chemical equilibria dynamic or static?

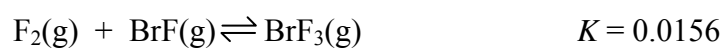
(c) Consider the chemical equilibrium given by equation (1):



(i) Give an expression for the thermodynamic equilibrium constant for reaction (1),  $K_1$ , in terms of the activities of the reaction components.

- (ii) Give an expression for  $K_1$  in terms of the partial pressures of the reaction components.

- (iii) Using the data below, calculate the value of  $K_1$ .



14. (9 marks)

- (a) Explain the difference between a *reaction quotient* and an *equilibrium constant*.

- (b) For the reaction given by equation (2), the equilibrium constant is  $K_2 = 1.05$  at  $25^\circ\text{C}$ .



- (i) Calculate the reaction quotient for a mixture of 1.0 atm  $\text{PCl}_5(\text{g})$ , 1.0 atm  $\text{PCl}_3(\text{g})$  and 0.5 atm  $\text{Cl}_2(\text{g})$ .

- (ii) For the mixture in (i), predict, *with reasoning*, the direction in which reaction (2) will proceed (at constant temperature and volume).

- (iii) Some time after preparing the mixture in (i), the total pressure was measured to be 2.70 atm. Calculate the partial pressures of each of the three reaction components.

- (iv) At the time of the measurement in (iii), has the reaction reached equilibrium? Give your reasoning.

**END OF PAPER**

(Physical Chemistry Formulae and Periodic Table on following pages)

## Physical Chemistry Formulae

$$PV = nRT$$

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

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

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

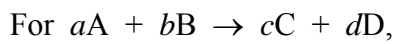
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$R$  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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