

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

Examination 2006

Prescription Number(s): CHEM 121

Paper Title: General Chemistry

Time Allowed: TWO HOURS

Number of pages: 17

Before commencing work, read the instructions on this page.

1. This is both your examination paper and your answer book. You may use the blank page opposite for any additional working pertaining to that question.
2. Please ensure that your name has been entered in the appropriate spaces above.
3. ANSWER **ALL** QUESTIONS.

Total marks = 100: you should allocate about 1 minute per mark.

4. It is good examination practice to read through the whole paper before you start answering the questions.

NOTE: There is a page of formulae and some constants and a periodic table after p15.

Please write your answers in the spaces provided

1/7	2/9	3/16	4/16	5/14	
6/10	7/6	8/6	9/8	10/8	Total

1. [7 marks]

a) Give the full electron configuration for the atoms or ions:

[Use, as an example, $1s^22s^22p^2$ for C ($Z=6$), as a model for the notation to be used in your answer.]

i) P ($Z = 15$)

ii) Mn^{2+} ($Z=25$)

iii) Cu ($Z=29$)

b) Draw the Lewis structure for methanoate ion $HCOO^-$. Are any two bonds of equal length? Explain.

2. [9 marks]

a) In the spaces below explain how hydrogen bonding in water plays an important role in moderating ocean temperature at different times of the year.

i) In **Summer**

ii) In **Winter**

b) Explain, using a diagram if necessary, why ice floats in liquid water.

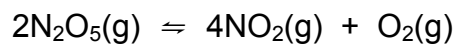
3 [16 marks]

Given the following data for a temperature of 298 K,

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
$\text{N}_2\text{O}_5(\text{g})$	-43.1	+113.9
$\text{NO}_2(\text{g})$	+33.18	+51.31

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

Using the data above answer the following questions about the reaction:



(a) Determine the direction in which the reaction is likely to proceed under standard conditions.

(b) Calculate the thermodynamic equilibrium constant, K , at 25°C .

(c) Calculate the standard entropy change, ΔS° , for the reaction. Comment on the sign of the standard entropy change.

(d) At what temperature ($^\circ\text{C}$) will a mixture of $\text{N}_2\text{O}_5(\text{g})$ and $\text{NO}_2(\text{g})$, both with partial pressures of 1 atmosphere, be at equilibrium?

4. [16 marks]

a) For the reaction: $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
the following data were obtained at 1100 K:

[NO] / mol L ⁻¹	[H ₂] / mol L ⁻¹	Initial rate / mol L ⁻¹ s ⁻¹
5.00×10^{-3}	2.50×10^{-3}	3.0×10^{-3}
15.00×10^{-3}	2.50×10^{-3}	9.0×10^{-3}
15.00×10^{-3}	10.0×10^{-3}	3.6×10^{-2}

i) Determine the order with respect to both NO and H₂

ii) What is the overall order

- iii) Write the rate law.
- iv) Calculate the rate constant.
- v) Calculate the initial rate of this reaction at 1100 K when
 $[\text{NO}] = [\text{H}_2] = 8.0 \times 10^{-3} \text{ mol L}^{-1}$.
- vi) If this reaction is carried out at constant volume and temperature, draw a graph showing the total pressure as a function of time. Assume the initial pressure is 1.00 kPa.

- b) For the reaction: $2\text{NOCl}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$,
the rate constants at 127°C and 177°C are 6.95×10^{-4} and
 $1.98 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ respectively. Calculate the activation energy for
the reaction.

5. [14 marks]

Given the following table of standard reduction potentials:

Reduction Half-reaction	E° / V
$\text{Cu}^{2+}(\text{aq.}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.337
$\text{Ni}^{2+}(\text{aq.}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Fe}^{2+}(\text{aq.}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq.}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.763

- Which is the strongest oxidising agent?
- Which is the strongest reducing agent?
- Which ions will Fe(s) reduce?
- Write down the cell diagram for a cell involving the nickel and zinc couples which has a positive standard cell potential. Calculate the standard cell potential for that cell.

- e) Calculate the equilibrium constant for the reaction of Fe(s) and Ni²⁺(aq.)
- f) Calculate the standard free energy change, ΔG° , for the reaction of Zn(s) and Cu²⁺(aq.)

6. [10 marks]

When 0.3 moles of gaseous butene (C_4H_8) is completely oxidised to form $H_2O(l)$ and $CO_2(g)$ in a constant volume bomb calorimeter, 818 kJ of heat are evolved at 298 K.

(a) Write a balanced equation for the oxidation of $C_4H_8(g)$.

(b) Calculate:

(i) q_V per mole for the oxidation of $C_4H_8(g)$.

(ii) ΔU° per mole for the oxidation of $C_4H_8(g)$.

(iii) ΔH° per mole for the oxidation of $C_4H_8(g)$.

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

- (iv) ΔH_f° (C₄H₈(g)) if ΔH_f° (H₂O)(l) = -285.8 kJ mol⁻¹ and ΔH_f° (CO₂(g)) = -393.5 kJ mol⁻¹.

7. [6 marks]

Seawater contains both calcium and magnesium cations with the following concentrations:

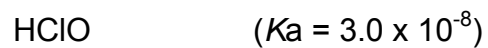
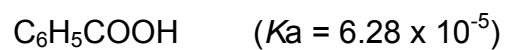
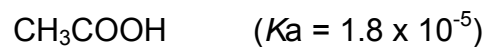
$$[\text{Ca}^{2+}] = 0.020 \text{ mol L}^{-1}; [\text{Mg}^{2+}] = 0.070 \text{ mol L}^{-1};$$

$$K_{\text{sp}} \text{ Ca(OH)}_2 = 5.5 \times 10^{-6} \quad K_{\text{sp}} \text{ Mg(OH)}_2 = 1.1 \times 10^{-11}$$

If NaOH is added to seawater, calculate the [OH⁻] at which each cation will precipitate.

8 [6 marks]

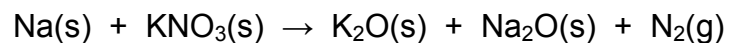
- a) Given that you have been asked to prepare a buffer with a pH of 5.0 which of the following acids (and its conjugate salt) would you use and why?



- b) Using the K_a value of 1.8×10^{-5} for acetic acid work out (in detail) a method, using a measuring cylinder, to prepare a buffer solution of pH = 4.90 using 0.1 mol L^{-1} acetic acid and 0.1 mol L^{-1} sodium acetate solutions.

9. [8 marks]

An important reaction in the operation of automobile air bags is the following reaction:



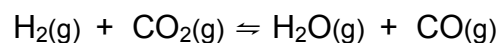
a) Use ion-electron half equations, balance the above equation. (You may include H^+ ions and H_2O even though they are not involved in the overall reaction)

b) Calculate the volume of nitrogen gas produced from 10.0g of KNO_3 at 20°C and 100 kPa pressure.

Data: $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$; $M(\text{KNO}_3) = 101.1 \text{ g mol}^{-1}$

10. [8 marks]

a) The equilibrium constant, K , for the reaction



is 4.4 at 2000K. **Calculate:**

i) ΔG° for the reaction at 2000K

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

ii) ΔG for the reaction at 2000K when the **initial** pressures are

$p(\text{H}_2) = 0.15 \text{ atm}$, $p(\text{CO}_2) = 0.83 \text{ atm}$, $p(\text{H}_2\text{O}) = 0.54 \text{ atm}$,

$p(\text{CO}) = 1.15 \text{ atm}$.

iii) In which direction does the spontaneous reaction occur at 2000K under the conditions given in (ii)?

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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