

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

End-of-Year Examinations 2007

Prescription Number(s): CHEM 115

Paper Title: General Chemistry C

Time Allowed: NINETY MINUTES

Number of pages: FIFTEEN

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 = 90: you should allocate 1 minute per mark.

NOTE: There is a periodic table on p15.

Please write your answers in the spaces provided

For examiners use only

1-3	4-6	7-8	9-11	TOTAL

1. (12 marks)

(a) Fill in the boxes to indicate the number of 4s and 3d electrons in each of the following species in their ground state:



(b) Which 3d transition element forms many compounds in the +I oxidation state?

(c) Which 3d transition element forms many compounds in both the +III and +VI oxidation states?

(d) Complete the following table (en = NH₂CH₂CH₂NH₂):

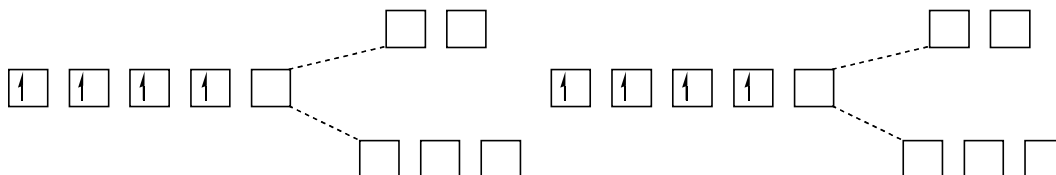
Property of the metal	[Fe(H ₂ O) ₅ (OH)] ²⁺	[MnO ₄] ⁻	PtCl ₂ (en) ₂
Oxidation state			
Coordination number		4	
Geometry			

2. (5 marks)

- (a) Sketch the intermediate for a dissociative substitution reaction of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with NH_3 .
- (b) What is the coordination number for the intermediate in an associative substitution reaction of an octahedral complex?
- (c) Describe how an *interchange substitution* mechanism differs from an *associative substitution* mechanism.

3. (5 marks)

On the crystal-field splitting diagram below, show the two possible ground-state d-electron configurations for a metal ion with four d electrons in an octahedral complex. After doing this, circle the terms beneath each configuration which correctly describe it.



low spin

high spin

diamagnetic

paramagnetic

likely to be found in complexes
with Br^- as the ligand

likely to be found in complexes
with CO as the ligand

low spin

high spin

diamagnetic

paramagnetic

likely to be found in complexes
with Br^- as the ligand

likely to be found in complexes
with CO as the ligand

4. (8 marks)

Ni^{2+} forms pale-coloured octahedral complexes with a range of ligands.

(a) Explain why the colours of the Ni^{2+} complexes vary as the ligands vary.

- (b) Explain why $[\text{Ni}(\text{en})_3]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ have similar blue colours, whereas $[\text{Ni}(\text{CN})_6]^{4-}$ is yellow. The table below should be of assistance.

Relationship of wavelength to colour

Wavelength absorbed (nm)	Colour observed
400 (violet)	Green-yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

5. (8 marks)

The concentration of Cu^{2+} in solution can be determined quantitatively by complexometric titration with EDTA in the presence of ammonia, with fast sulfon black F as an indicator (In). The indicator binds as a bidentate ligand to Cu^{2+} ions.

The colours of the various species are:

$[\text{Cu}^{2+}\text{-In}]$ complex:	red
Free In:	dark yellow
$[\text{Cu}(\text{NH}_3)_4]^{2+}$:	dark blue
$[\text{Cu}(\text{EDTA})]^{2-}$:	sky blue

(a) Which of the three Cu^{2+} complexes ($[\text{Cu}^{2+}\text{-In}]$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Cu}(\text{EDTA})]^{2-}$), has the largest K_f value and which has the smallest?

Largest K_f :

Smallest K_f :

(b) Explain why this order of K_f values in (a) is essential for the titration to be successful.

(c) List the species in solution immediately before the endpoint and immediately after the endpoint:

Before endpoint:

After endpoint:

What is the colour change at the endpoint?

From:

To:

(d) What is the ratio (mol Cu^{2+} : mol EDTA^{4-}) at the endpoint? Circle the correct answer.

1:1

1:3

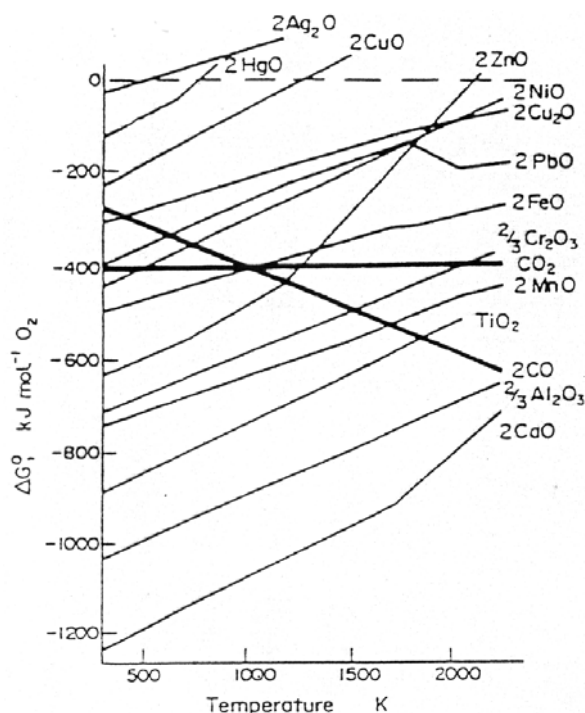
1:6

3:1

6:1

6. (10 marks)

The Ellingham diagram, shown below, for the formation of oxides should be helpful for answering this question.



- (a) Explain why the line on the Ellingham diagram labelled 'TiO₂' has a positive slope, and the line labelled '2CO' has a negative slope.
- (b) Calculate ΔG° per mol O₂ for the formation of chromium metal from its oxide using carbon as the reducing agent at $T = 1700$ K.

(c) Is the formation of chromium metal from its oxide using carbon as the reducing agent at 1700 K spontaneous? Explain your answer.

(d) Above what temperature is the reduction of MnO by carbon thermodynamically favourable? Explain your answer.

7. (7 marks)

- (a) Explain why the ionisation energy of B is less than that of C.
- (b) Explain why the ionisation energy of F is greater than that of Cl.
- (c) Explain why the ionisation energy of F^- is less than that of F.
- (d) Explain why the bond energy of a double bond between two O atoms is greater than that between two S atoms.
- (e) Explain why the bond energy of C=N is much greater than N=N (640 versus 450 kJ/mol) whereas C≡C is similar to N≡N (960 versus 950 kJ/mol).

8. (5 marks)

Put the following list of atoms/ions in order of increasing size. Rationalise your chosen order:

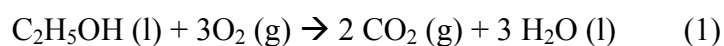
S, Cl, Br, Cl^- , Na^+

9. (12 marks)

(a) What is the definition of a state function?

(b) Give the names and symbols for two examples of thermodynamic state functions

- (c) For the combustion of ethanol (reaction (1)), calculate ΔH° at 298 K using the thermodynamic data provided.



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH} (\text{l})$	-277.0	-174.2
$\text{CO}_2 (\text{g})$	-393.5	-394.4
$\text{H}_2\text{O} (\text{l})$	-285.8	-237.2

- (d) Calculate ΔG° for reaction (1).

- (e) Is reaction (1) a spontaneous process at 298 K? Give a reason for your answer.

- (f) If $\Delta G^\circ = 0$ for a reaction, what can you say about the reactants and products of that reaction?

10. (6 marks)

- (a) State the second law of thermodynamics in words and provide an equivalent mathematical statement.

- (b) Does the change in the entropy of a system, ΔS_{sys} , have to be positive for a reaction to be spontaneous? Explain your answer.

11. (12 marks)

(a) Describe, or sketch, the standard hydrogen electrode (SHE) and explain what it is used for.

(b) An electrochemical cell is established at 298 K using the following electrodes, which have the indicated standard reduction potentials:

$$E^{\circ} (\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V and } E^{\circ} (\text{Cu}^{2+} / \text{Cu}) = 0.34 \text{ V.}$$

(i) Give the standard cell potential, E°_{cell}

(ii) Draw the conventional cell diagram and indicate clearly the direction of electron flow in the external circuit when the current is drawn.

(iii) Give the half cell reactions.

- (iv) Give the overall cell reaction.
- (c) Write an equation that describes the EMF of this cell under non-standard conditions.
- (d) For the cell reaction given in (b) (iv), **calculate** the EMF at 298 K when $[\text{Fe}^{3+}] = 0.01 \text{ mol L}^{-1}$, $[\text{Fe}^{2+}] = 0.05 \text{ mol L}^{-1}$ and $[\text{Cu}^{2+}] = 0.05 \text{ mol L}^{-1}$.
{Data: $RT/F = 0.0257 \text{ V}$ at 298 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
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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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