

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

End-of-Year Examinations 2005

Prescription Number(s): CHEM 112

Paper Title: General Chemistry B

Time Allowed: 90 MINUTES

Number of pages: SIXTEEN

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 at the end of this paper.

Please write your answers in the spaces provided

For examiners use only

1-3	4-6	7-9	10-16	Total

TURN OVER

1. (12 marks)

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



- (b) Give the oxidation state (oxidation number) of the metal in:



- (c) (i) Give the formula and colour of the cobalt species that forms when CoCl_2 is dissolved in water.

Formula:

Colour:

- (ii) Give the formula and colour of the cobalt species that forms when concentrated HCl is added to the solution in part (i).

Formula:

Colour:

- (d) Draw the structure of $[\text{Co}(\text{EDTA})]^-$ showing the donor atoms and linkages between them.
- (e) Write a balanced half equation describing permanganate, MnO_4^- , acting as an oxidizing agent in acid solution.

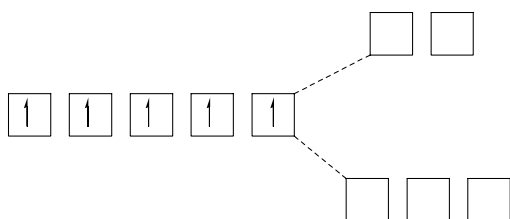
2. (5 marks)

An example of the chelate effect is the higher stability of $[\text{Ni}(\text{en})_3]^{2+}$ compared with $[\text{Ni}(\text{NH}_3)_6]^{2+}$. (Note: en is ethylenediamine or ethane-1,2-diamine)

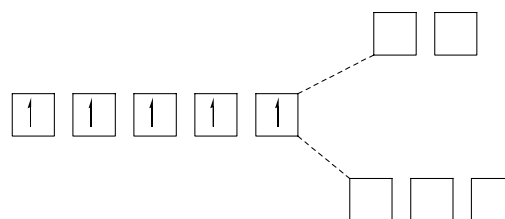
Use entropy arguments to account for the relative stabilities of $[\text{Ni}(\text{en})_3]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

3. (5 marks)

On the diagram below, show the two possible d-electron configurations for an octahedral complex with five d electrons. 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 F^- as the ligand
 likely to be found in complexes
 with CN^- as the ligand
 likely to form colourless complexes



low spin
 high spin
 diamagnetic
 paramagnetic
 likely to be found in complexes
 with F^- as the ligand
 likely to be found in complexes
 with CN^- as the ligand
 likely to form colourless complexes

4. (6 marks)

Cisplatin (*cis*-PtCl₂(NH₃)₂) is used as a chemotherapy agent to treat some cancers.

- (a) Draw the structure of cisplatin. What is its geometry?
- (b) Describe the proposed mode of action of cisplatin as a cancer-treatment drug (you may wish to refer to the hydrolysis reaction below).



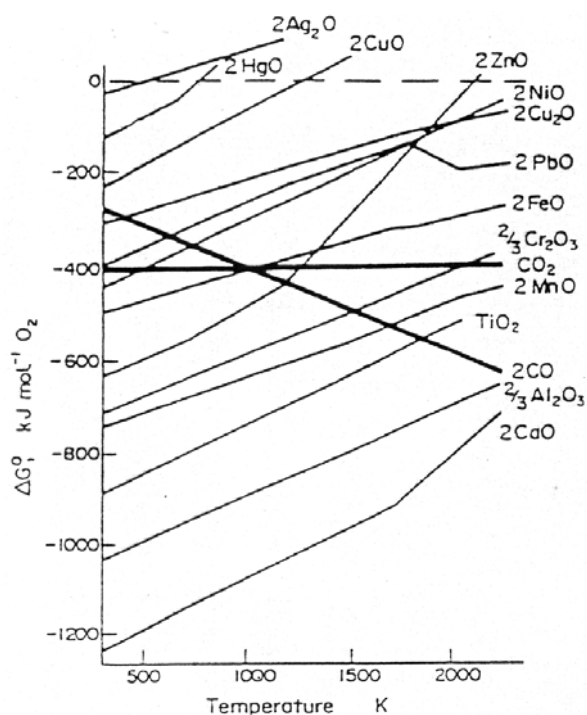
5. (7 marks)

Ni²⁺ forms pale-coloured octahedral complexes with a range of ligands.

- (a) Explain why the colours of the Ni²⁺ complexes vary as the ligands vary;
- (b) Explain why [Ni(en)₃]²⁺ and [Ni(NH₃)₆]²⁺ have similar colours whereas the colour of [Ni(CN)₆]⁴⁻ is very different. (Note: en is ethylenediamine or ethane-1,2-diamine)

6. (7 marks)

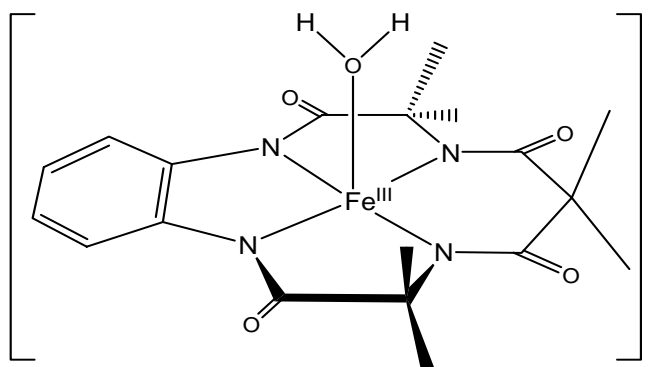
The Ellingham diagram shown below for the formation of metal and non-metal oxide will be helpful for answering this question.



- Explain why the line on the Ellingham diagram labelled '2MnO' has a positive slope, and the line labelled '2CO' has a negative slope.
- Estimate ΔG° per mol O_2 for the formation of silver metal from its oxide by thermal decomposition of the oxide at $T = 1000$ K.
- Is the process in (b) above spontaneous? Explain your answer.
- Why is thermal decomposition **not** used to extract iron from its oxide?

7. (8 marks)

Three bleaches that can be used in paper making are Cl_2 , ClO_2 and H_2O_2 (with a TAML activator, see structure below).



- (a) What type of reaction is involved in bleaching?
- (b) Briefly describe the advantage(s) and disadvantage(s) of each bleaching system for paper making:

Cl_2 :

ClO_2 :

H_2O_2 /TAML activator:

8. (3 marks)

In the compound CaH_2 :

- (a) Which has higher electronegativity, Ca or H?
- (b) How can the ionic character of CaH_2 be demonstrated?

9. (7 marks)

- (a) Define the term **first ionisation energy** of an element.
- (b) Briefly describe and account for the periodic trends in first ionisation energy.
- (c) How does ionisation energy vary with oxidation state? Give an explanation for this.

11. (4 marks)

What is the electrophilic species produced from the following combinations of reagents:

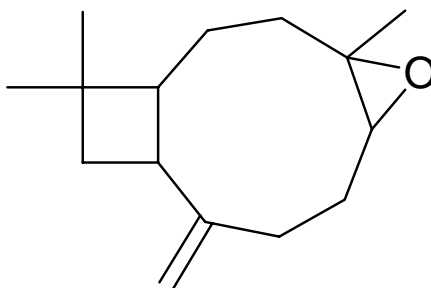
(i) conc. H_2SO_4 and conc. HNO_3 ? Ans:

(ii) CH_3COCl and AlCl_3 ? Ans:

Draw the structures of the **three** resonance contributors to the Wheland intermediate involved in the electrophilic **nitration** of benzene.

12. (3 marks)

The sesquiterpene **caryophyllene oxide** (below) is found in many plants, such as thyme.

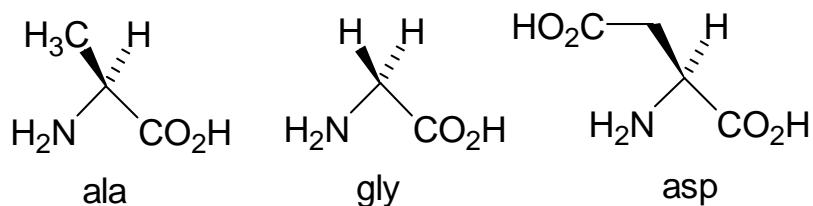


caryophyllene oxide

Identify clearly the isoprene units in the structure above. Identify with arrows the bonds that represent the head-to-tail linkages. Circle the bond that represents the extra C-C cross link.

13. (4 marks)

The structures of the amino acids alanine (ala), glycine (gly) and aspartic acid (asp) are shown below.



(a) Draw the structures of aspartic acid in the form you would expect to predominate at low pH (e.g. pH = 2) and at high pH (e.g. pH = 12)?

Low-pH form

High-pH form

(b) Draw the **structure** of the tripeptide gly-asp-ala. Indicate with arrows any peptide bonds in the structure and give the **name** of an isomeric tripeptide with a different sequence.

Structure of gly-asp-ala

Name of isomer

14. (3 marks)

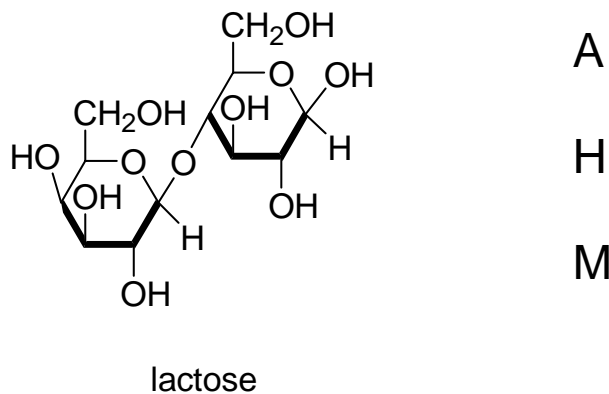
The structure of the disaccharide lactose is shown below.

Is lactose formed from two identical monosaccharides (circle the correct answer)?

Yes

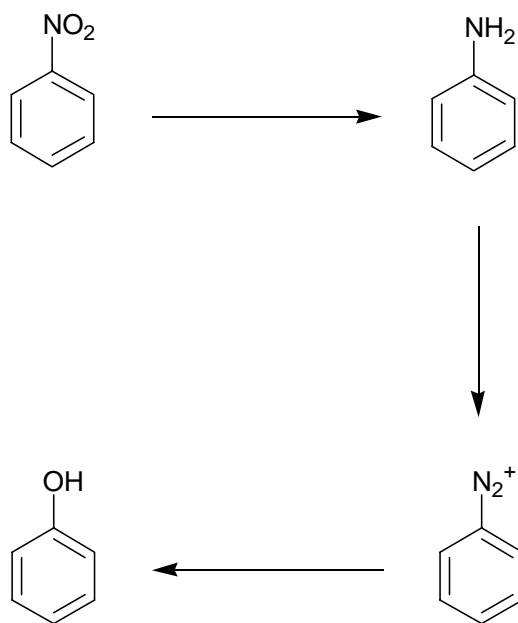
No

In the diagram below draw arrows to an acetal carbon (A), a hemiacetal carbon (H) and the carbon that undergoes a change of stereochemistry during the process of mutarotation (M).



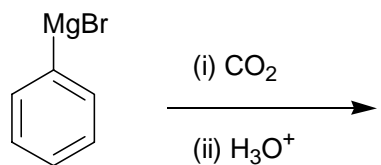
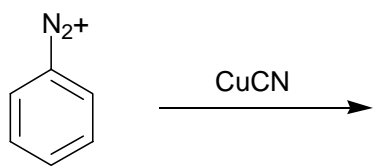
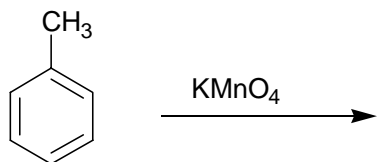
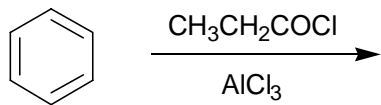
15. (3 marks)

Next to each arrow, indicate the reagents required to carry out the following reaction sequence.



16. (4 marks)

Give the structures of the products of the following reactions.



TURN OVER

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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