Full Name: .....

Student ID #: .....

UNIVERSITY OF CANTERBURY

End-of-Year Examinations 2007

Prescription Number(s):	CHEM 112
Paper Title:	General Chemistry B

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	9-14	**TOTAL**

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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:

V(III) [Ar] 4s☐ 3d☐

Ni(0) [Ar] 4s☐ 3d☐

(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 = $NH_2CH_2CH_2NH_2$):

Property of the metal	$[Fe(H_2O)_5(OH)]^{2+}$	$[MnO_4]^-$	$PtCl_2(en)_2$
Oxidation state			
Coordination number		4	
Geometry			

2. (5 marks)

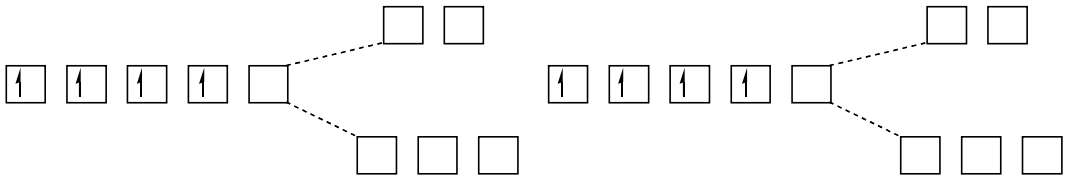
(a) Sketch the intermediate for a dissociative substitution reaction of $[Co(H_2O)_6]^{2+}$ with NH_3.

(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	low spin
high spin	high spin
diamagnetic	diamagnetic
paramagnetic	paramagnetic
likely to be found in complexes with Br^- as the ligand	likely to be found in complexes with Br^- as the ligand
likely to be found in complexes with CO 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 $[Ni(en)_3]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have similar blue colours, whereas $[Ni(CN)_6]^{4-}$ 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:

$[Cu^{2+}\text{-In}]$ complex:	red
Free In:	dark yellow
$[Cu(NH_3)_4]^{2+}$:	dark blue
$[Cu(EDTA)]^{2-}$:	sky blue

(a) Which of the three Cu^{2+} complexes ($[Cu^{2+}\text{-In}]$, $[Cu(NH_3)_4]^{2+}$ and $[Cu(EDTA)]^{2-}$), 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?

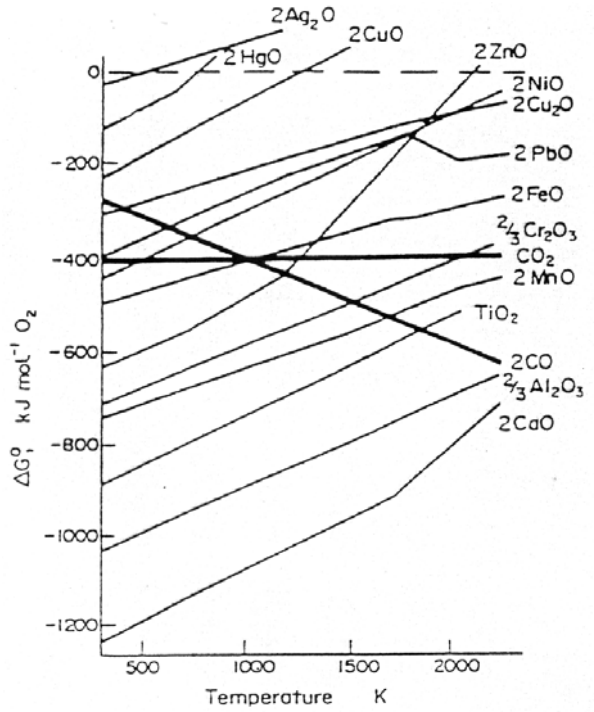
From: To:

(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 'TiO_2' has a positive slope, and the line labelled '2CO' has a negative slope.

(b) Calculate $\Delta G°$ per mol O_2 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).

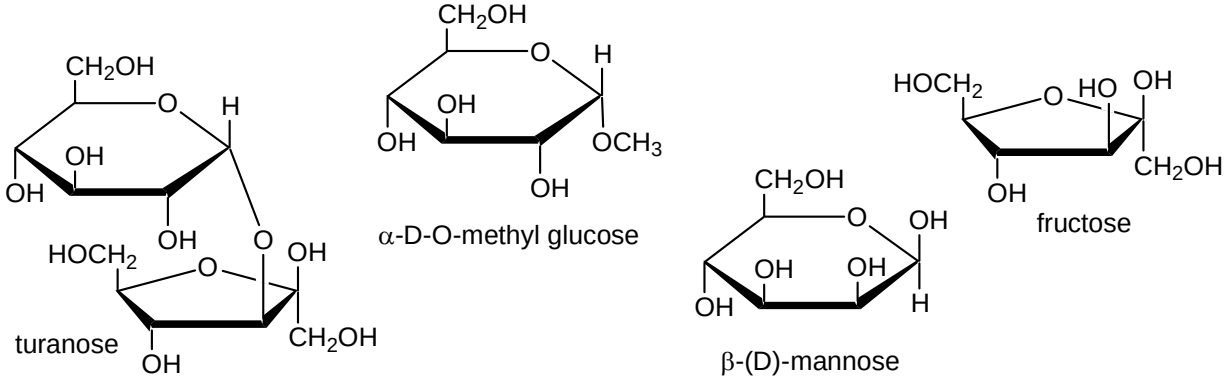
8. (5 marks)

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

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

9. (5 marks)

(a) For the sugars below, circle any acetal carbons



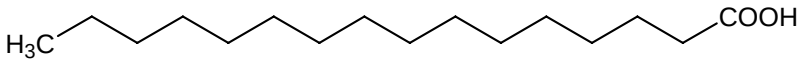
(b) Briefly explain why α-D-O-methyl glucose does not undergo mutarotation but β-D- mannose does.

10. (7 marks)

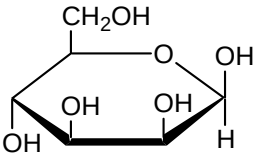
Shown below are a selection of natural products (**A** – **L**)

Which of these is:

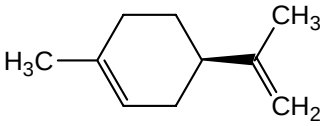
(a)	a 16:1 fatty acid	**Ans:**
(b)	a ketotetrose	**Ans:**
(c)	a disaccharide	**Ans:**
(d)	a tetrapeptide	**Ans:**
(e)	a monocyclic monoterpene	**Ans:**
(f)	a triglyceride	**Ans:**
(g)	a sesqiterpene	**Ans:**



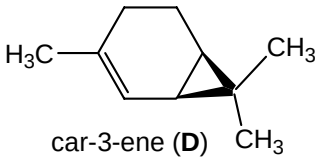
palmitic acid (**A**)



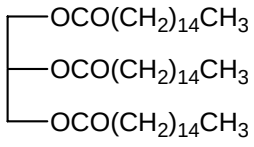
β-(D)-mannose (**B**)



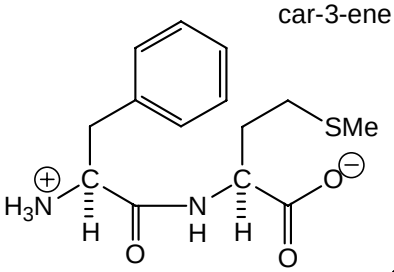
limonene (**C**)



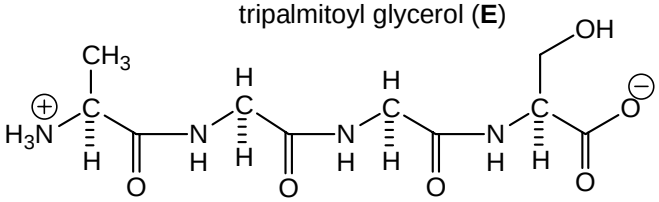
car-3-ene (**D**)



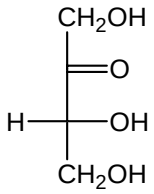
tripalmitoyl glycerol (**E**)



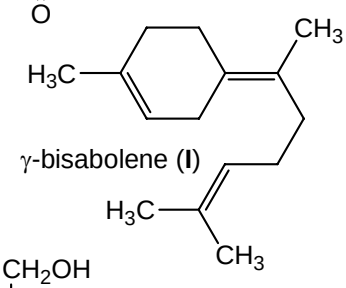
phe-met (**F**)



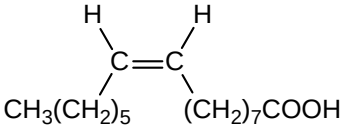
ala-gly-gly-ser (**G**)



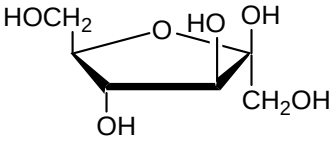
D-erythrulose (**H**)



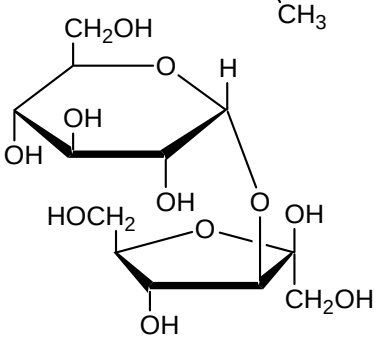
γ-bisabolene (**I**)



palmitoleic acid (**J**)



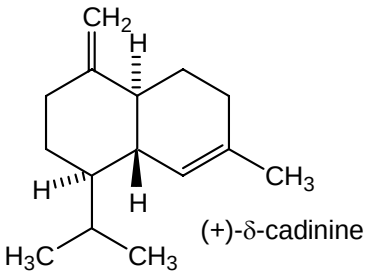
fructose (**K**)



turanose (L)

11. (5 marks)

(+)-δ-Cadinine is a component of the essential oils produced by cotton plants.



(+)-δ-cadinine

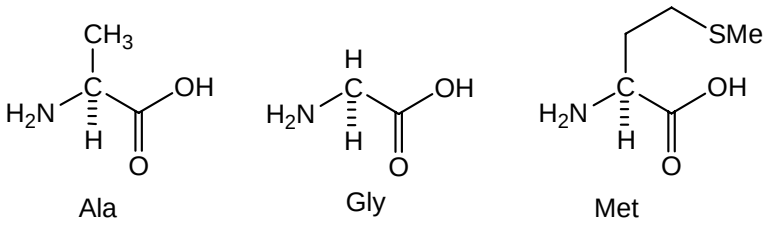
(a) Label this structure to clearly identify the C5 units.

(b) Use arrows to identify the bonds that represent head-to-tail linkages and label each end of the bond as h or t.

(c) Circle the bond(s) that represent the extra C-C cross-link(s).

12. (4 marks)

The structure of the amino acids glycine (Gly), alanine (Ala) and methionine (Met) are shown below:



(a) Draw the structure of methionine that predominates in aqueous solution at pH=7 and briefly explain why it is not the same as the one drawn above.

(b) Draw the structure of the tripeptide Met-Gly-Ala.

(c) Use three letter amino acid abbreviations to write out the structure of a constitutional isomer of Met-Gly-Ala.

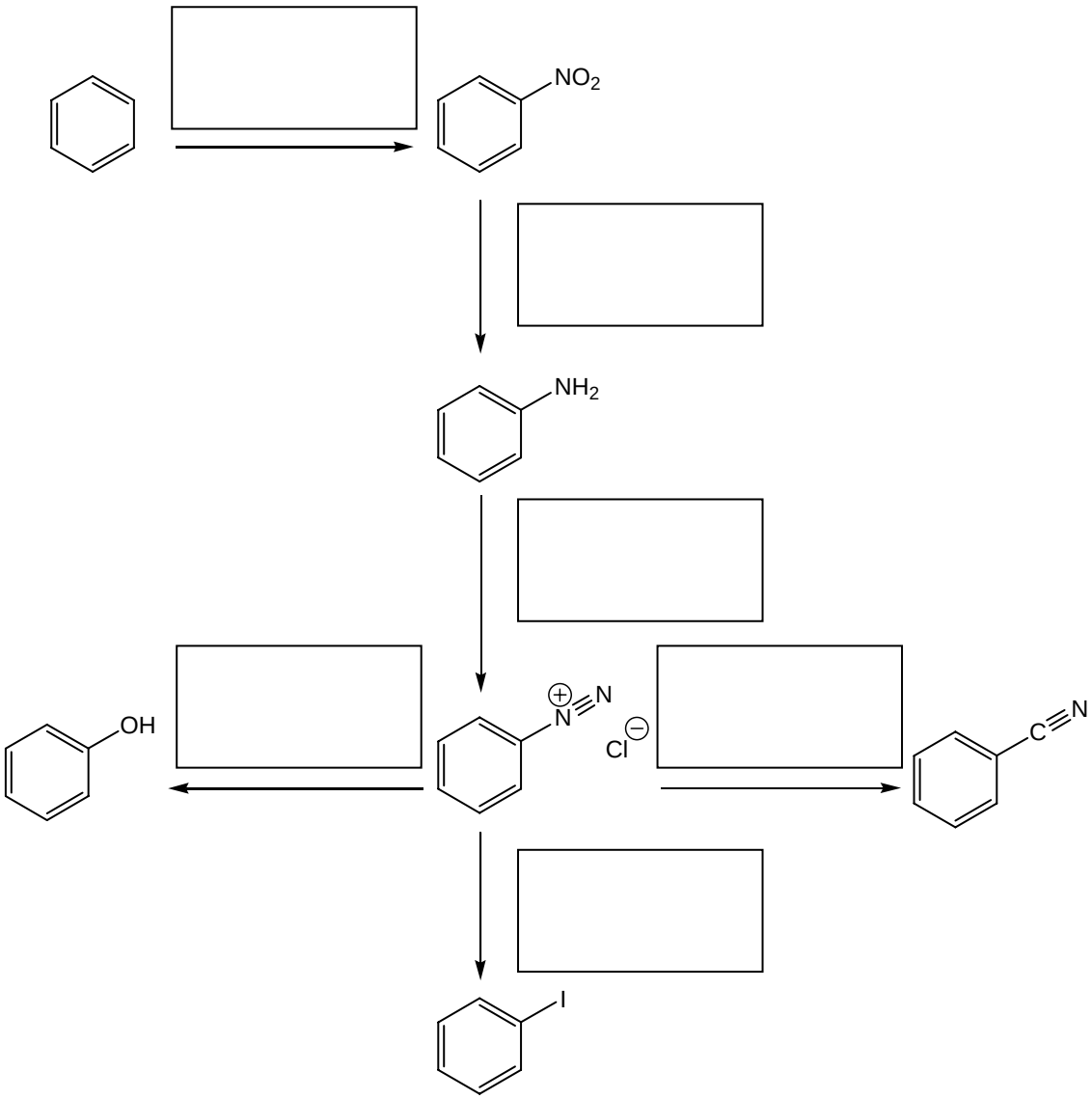
13. (5 marks)

(a) Draw out the equation for the reaction that takes place when 1 mole equivalent of chlorine (Cl_2) reacts with benzene in the presence of a $FeCl_3$ catalyst and briefly explain why the reaction is a substitution, rather than an addition, reaction.

(b) Draw out a mechanism for the reaction in (a) and briefly explain why the $FeCl_3$ catalyst needed.

14. (4 marks)

Give reagents for **four** of the transformations on the following scheme.



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

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)

END OF PAPER

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