Full Name: .....

Student ID #: .....

Signature: .....

UNIVERSITY OF CANTERBURY

End-of-Year Examinations 2009

Prescription Number(s):	CHEM 112 CHEM 115
Paper Title:	General Chemistry B General Chemistry C

Time Allowed: $2^1/_2$ HOURS

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 = 120

NOTE: There is a periodic table on p16.

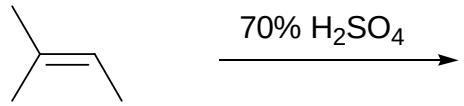
Please write your answers in the spaces provided

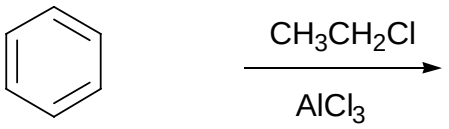
For examiners use only

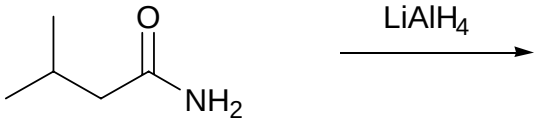
1-7	8-11	12-14	**TOTAL**

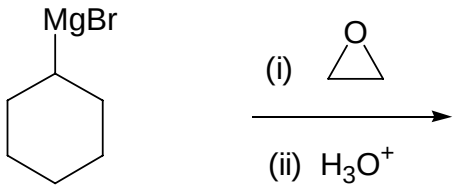
Question 1 *(5 marks)*

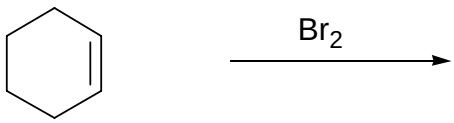
Draw the structures of the products of the following reactions.











Question 2 *(4 marks)*

What **reagents** are used for the following reactions?

(a) Anti-Markovnikov addition of water to an alkene. Ans:

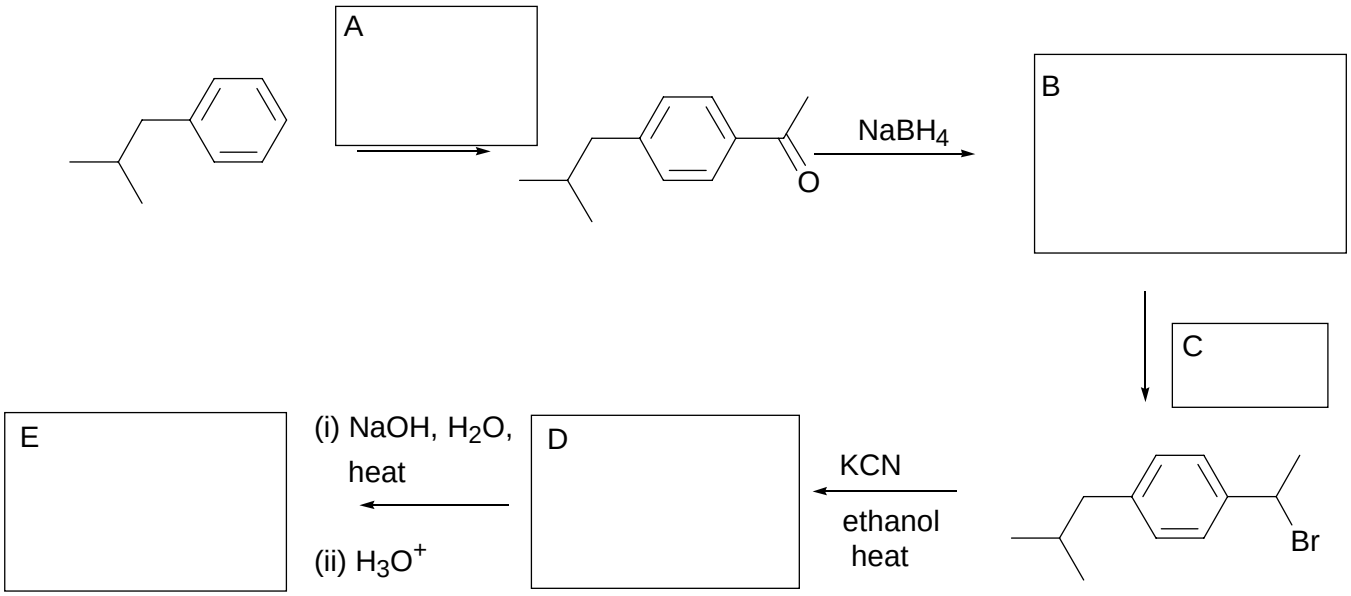
(b) Conversion of an alcohol to an alkyl chloride. Ans:

(c) Conversion of nitrobenzene to aniline. Ans:

(d) Conversion of aniline to a diazonium salt. Ans:

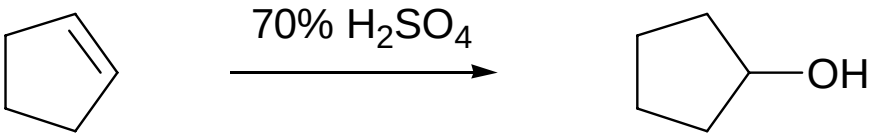
Question 3 *(5 marks)*

Shown below is a synthesis of Ibuprofen (Nurofen). In the boxes provided draw the missing reagents (A and C) and structures (B, D and E).



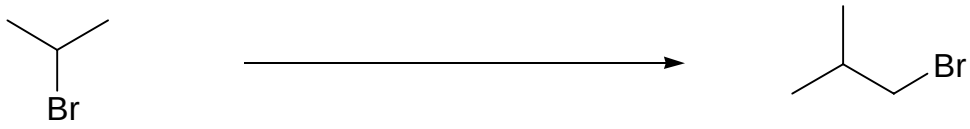
Question 4 *(6 marks)*

Draw the full mechanism for the following reaction, using curly arrows to show all electron movement.

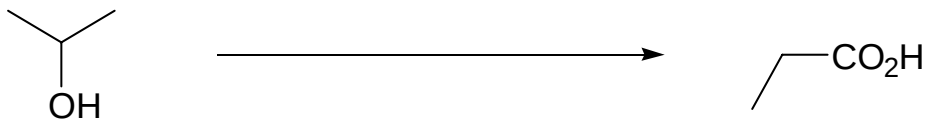


Question 5 *(12 marks)*

For each of the following transformations, draw a reaction scheme that could be used to convert the starting material to the final product. For each step of the reaction sequence, specify all necessary reagents and reaction conditions.

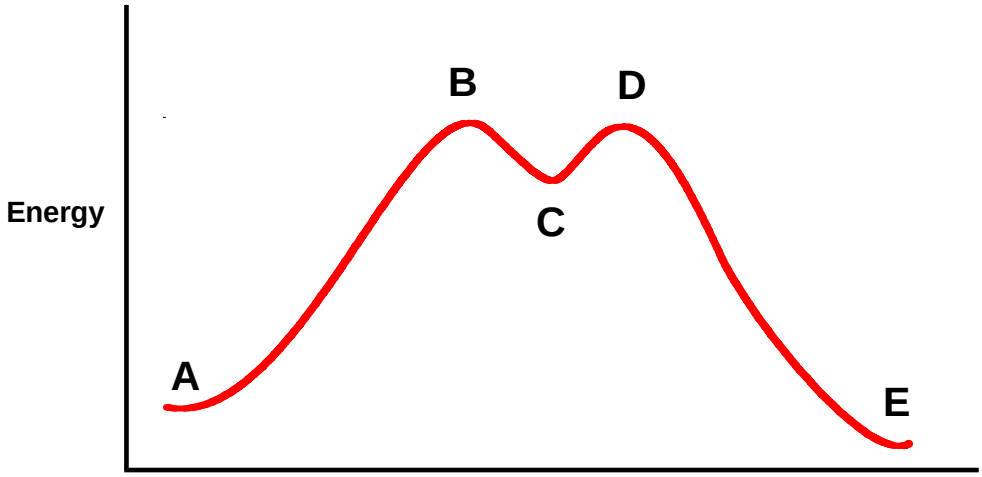
(a) 

(b) ethanal ⟶ ethanamide

(c) 

Question 6 *(9 marks)*

Shown below is a typical energy profile diagram for a chemical reaction.



(a) If this was for a nucleophilic substitution would it be S_N1 or S_N2? Ans:

(b) What type of species would be represented by C? Ans:

(c) The formation of which transition state would determine the rate? Ans:

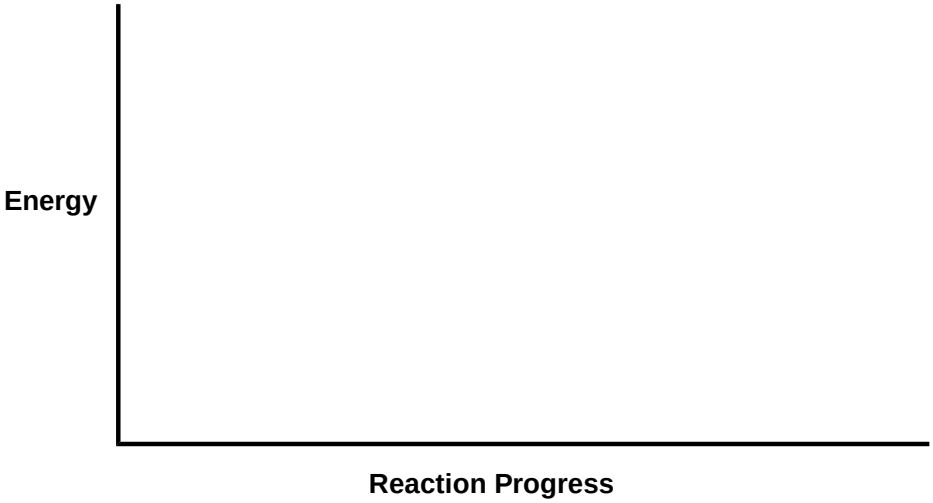
(d) Would the nucleophile be involved in the step leading from A to C? Ans:

(e) What type of alkyl halide would react fastest by this mechanism? Ans:

(f) If A was a single enantiomer in which the halide was attached to a chiral centre what would be the stereochemistry of E? Ans:

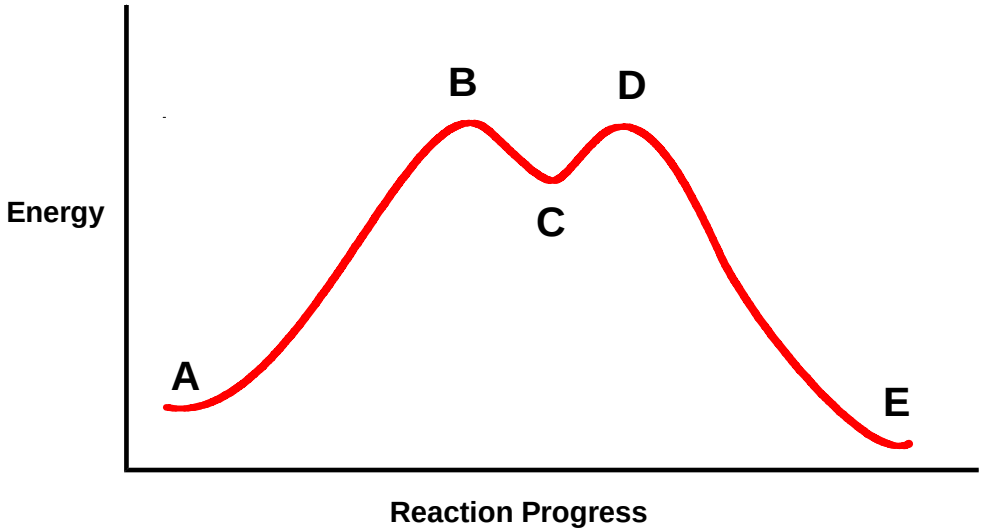
(g) What would happen to the rate of this reaction if the concentration of the nucleophile was doubled? Ans:

(h) In the diagram below draw the corresponding profile for the other type of nucleophilic substitution mechanism.



Question 7 *(4 marks)*

Shown below is a typical energy profile diagram for a chemical reaction.



(a) If this was for the bromination of benzene, what would be the structure of E?

(b) If this was for the nitration of benzene, what would be the structure of C (show all resonance contributors)?

(c) In the nitration of benzene what is the electrophile and how is it generated?

Question 8 *(10 marks)*

(a) Circle **all** the transition elements in the list below (note: marks will be deducted for wrong answers).

Cr Ce Zn Sc Ag Os Hg

(b) Give the electron configurations of the following species in their ground electronic state (note you should start from the configuration of the appropriate noble gas, e.g. [Ar]…..):

V(0):

Ni(II):

Cu(0):

(c) Explain why transition metal ions in an oxidation state greater than III (+3) are not found as aqua complexes (i.e. with H_2O as a ligand). Include in your answer the formula of a species which illustrates this observation.

(d) For the complex $[Co(en)_3]^{3+}$, where en is ethylenediamine (ethane-1,2-diamine):

(i) What is the oxidation state (oxidation number) of Co?

(ii) What is the coordination number of Co?

(iii) What are the donor atoms?

(iv) What is the denticity of en?

(v) What is the geometry of the complex?

Question 9 *(10 marks)*

Gadolinium(III) complexes are used as contrast agents in magnetic resonance imaging (MRI).

(a) Explain why Gd(III) complexes have a large magnetic moment.

(b) The complex $[Gd(DTPA)(H_2O)]^{2-}$ (DTPA is diethylenetriaminepentaacetate) is a widely used contrast agent. Draw the structure of DTPA, showing the donor atoms and how they are linked together (use ⌒ to show the links; it is not necessary to show all atoms in the structure).

(c) The complex $[Gd(EDTA)(H_2O)_3]^-$ cannot be used as a contrast agent because it dissociates and releases the highly toxic Gd(III) ion. Formation constant (K_f) values for the complexes are: K_f ($[Gd(DTPA)(H_2O)]^{2-}$) = $10^{22.5}$ and K_f ($[Gd(EDTA)(H_2O)_3]^-$) = $10^{17.4}$

Providing full reasoning, account for this order of K_f values

Question 10 *(8 marks)*

(a) Define, in brief, the term **spectrochemical series**.

(b) Explain the general observation that, for a given transition metal ion, octahedral complexes of en and NH_3 have similar colours whereas the colour of the cyano (CN^-) complex is very different. Your answer should include a brief description of the origin of the pale colours of transition metal complexes. (Note: en is ethylenediamine (ethane-1,2-diamine)).

(c) Explain why complexes and compounds of Cu(I) are usually colourless.

Question 11 *(6 marks)*

Cisplatin (*cis*-$PtCl_2(NH_3)_2$) is used as a chemotherapeutic 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.

Question 12 *(8 marks)*

(a) For each set of atoms/ions given below, circle the one with the lowest ionization potential:

(i) F F^- F^+

(ii) N N^+ N^{2+}

(iii) Br^- Cl^- I^-

(iv) N O F

(v) Si Al P

(b) Explain why the elements of groups 2 and 18 have low electron affinities relative to the elements of the groups around them.

Question 13 *(23 marks)*

(a) (i) Give the most common oxidation state(s) for each of the following elements:

(A) Ge

(B) Bi

(C) Al

(ii) Give the formulae for TWO indium chlorides.

(b) Write a balanced equation for the reaction of Cl_2 with cold aqueous NaOH to give NaOCl(aq) and NaCl(aq). Indicate the oxidation state of Cl in the reactant and products.

(c) Draw Lewis dot diagrams for each of the following molecules (draw the resonance structures where appropriate):

(i) SO_2

(ii) IF_5

(iii) NO_2

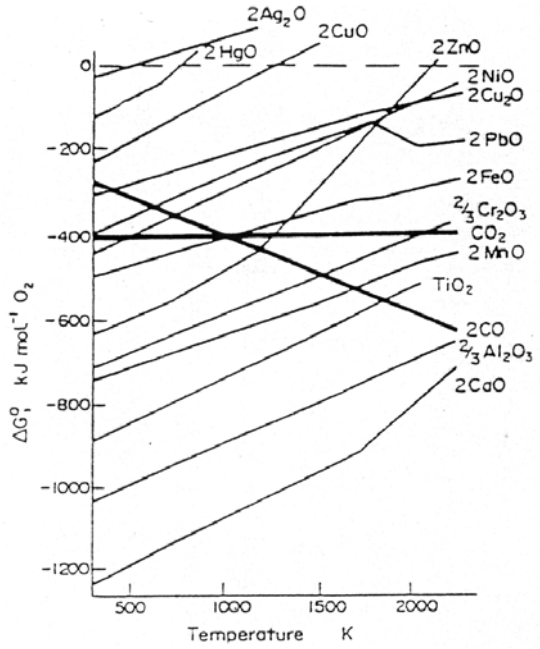
(d) Indicate the atomic formal charges on your answer to (i).

(e) What is the shape of IF_5?

(f) Why is NO_2 stable as a monomer?

Question 14 *(10 marks)*

The Ellingham diagram shown below will be useful for answering this question.



(a) Explain why the line on the Ellingham diagram labeled "TiO_2" has a positive slope, whereas the line labeled "CO_2" has a zero slope.

(b) Estimate $\Delta G°$ per mol O_2 for the formation of silver metal from its oxide by thermal decomposition of the oxide at T = 1000 K.

(c) Estimate $\Delta G°$ for the reduction of iron oxide by manganese at 1000 K.

Question 14 continued on following page

Question 14 continued

(d) What is $\Delta G°$ for the reduction of iron oxide by manganese at 1500 K?

(e) Why is the reduction of iron oxide to iron not usually carried out using Mn?

END OF PAPER
(Periodic Table on following page)

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)