JAMES COOK UNIVERSITY

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SCHOOL OF PHARMACY AND MOLECULAR SCIENCES
Chemistry Department

STUDY PERIOD 1 EXAMINATIONS 2007
CAMPUS: Cairns

No of pages including front page, exam paper and any attachments: 13
This paper must be handed in at the end of the Examination: Yes
Release to Library: No

STUDENT NAME:
(*block letters*)

STUDENT NUMBER:

SUBJECT CODE: CH1012:03

SUBJECT NAME: MOLECULAR CHEMISTRY

EXAMINER: Dr Michael Liddell **PHONE NO:** (07) 4042 1275

EXAMINER/CONTACT PERSON FOR ENQUIRIES ON DAY OF EXAM: **EXT. WORK:** 1275
Dr Michael Liddell

DURATION OF EXAMINATION (hours): TWO (2) HOURS

PERUSAL TIME (minutes): FIFTEEN (15) MINUTES

TOTAL NUMBER OF QUESTIONS: 27

INSTRUCTIONS TO STUDENTS:
The exam is composed of two sections:

Section A - Multiple choice - 22 questions - 33%
Section B - Short answer - 5 questions - 67%

Total marks for paper = 100
Answer **ALL** questions. All questions are **not** of equal value.
Timings are indicated to allow approximately 15 minutes of check-over time.

MATERIALS TO BE SUPPLIED BY EXAMINATION SECTION:
Examination Booklets required (Yes/No) Yes
Scanner Sheets required (Yes/No) Yes: a - e ☒

STANDARD MATERIALS PERMITTED IN AN EXAMINATION ROOM ARE:
Pencils, pens, erasers, white-out, rulers

ADDITIONAL MATERIALS STUDENTS MAY USE:
Scientific calculator with no text storage facilities.

Access to a dictionary:

- **English** **Yes** ☒ **or** **No** ☐
- **Bilingual English translation** **Yes** ☒ **or** **No** ☐

SECTION A

MULTIPLE CHOICE QUESTIONS (EACH QUESTION IS WORTH 1.5 MARKS). ANSWER ALL QUESTIONS – SHADE WITH A PENCIL THE MOST CORRECT ANSWER ON THE MULTICHOICE SCANNER SHEET.
Timing: you should complete the multi-choice section in 32 minutes (≈ 1.5 minutes per question).

SECTION B

SHORT ANSWER QUESTIONS. (MARKS FOR EACH QUESTION ARE AS INDICATED) ANSWER EACH OF THE FIVE (5) QUESTIONS.

Question 1

Timing: you should complete this question in 6 minutes.

The arrangement of the periodic table allows for clear trends in physical properties and chemical reactivity to be discerned as we move from the left-hand side to the right-hand side of a period.

- Explain the trend in atomic size on going across **Period 3**.
- Illustrate how the acid-base properties of the **metal oxides** vary on going across **Period 3** from Group IA to VIA and provide a justification for the trends observed.

(6 marks)

Question 2

Timing: you should complete this question in 13 minutes.

(a) Werner developed the concept of coordination compounds studying cobalt compounds such as

$[Co(NH_3)_5Br]Cl_2$. Using $[Co(NH_3)_5Br]Cl_2$ as an example define the terms **oxidation state** and **coordination number** as it applies to the cobalt ion in this coordination complex.

- Draw (in 3D perspective) a **coordination-sphere isomer** of the above complex.
- Propose a related complex (same metal and charge on the complex as $[Co(NH_3)_5Cl]Cl_2$) that contains a **bidentate ligand**.
- What is a **chelate ring**?

(4 marks)

(b) Give **systematic names** for the following compounds:

- $[Mo(NH_3)_4(CN)Cl]Br$
- $K_2[FeF_4]$

Provide a **molecular formula** for the following complex:

- sodium hexacyanomanganate(II)

(4 marks)

(c) For the following complex **identify** and **draw** illustrative examples of each the following types of isomers: coordination-sphere isomers, linkage isomers, geometric isomers, optical isomers – if they are valid possibilities for the complex.

- $[Ni(NH_3)_2Br(OH)]$
- Provide **systematic names** for the isomers.
- Provide an electronic **configuration** for nickel.

(4 marks)

Question 3

Timing: you should complete this question in 16 minutes.

(a) Real gases behave somewhat differently to ideal gases under conditions of high pressure and low temperature and many have an appreciable solubility in water.

- The **van der Waals forces** are responsible for the deviations from ideality, list these forces and explain their significance with respect to the **van der Waals equation**.

(3 marks)

(b) Careful control of physical conditions, in particular pressure, will generally determine if a pure

solid in a closed system will boil or sublime as the temperature is increased.

- Calculate the temperature at which *n*-butanol will boil at a pressure of 2600 Pa, if the normal boiling point is 118^{o}C. ΔH_{vap} (*n*-butanol) = 44.5 kJ mol^{-1}.
- Draw a **phase diagram for H_2O** and use it to illustrate how the process of **freeze drying** occurs.

(5 marks)

(c) Describe the **metallurgical processes** involved in the conversion of bauxite ore which is mined at Weipa into **aluminium** metal which is smelted at Gladstone.

- Why is electricity used for smelting aluminium rather than using a simple blast furnace such as that used for producing pig-iron?

(4 marks)

(d) (i) **Molecular orbital (MO) theory** is the area of quantum mechanics that is concerned with the description of the electronic structure of molecules.

- For a single electron in the second shell of an oxygen atom provide a **reasonable set of values** for the quantum numbers that specify this electron.
- Draw a complete **molecular orbital diagram** for the diatomic molecule O_2
- Is this molecule likely to be **paramagnetic**? - justify your answer.

(ii) Extension of MO theory to solids results in band theory. Use **band theory** to discuss the main differences between **intrinsic** and **extrinsic semiconductors**?

(4 marks)

Question 4

Timing: you should complete this question in 16 minutes.

(a) Identify the following unknown organic compound on the basis of the **analytical** and **spectroscopic data** provided and justify your answer.

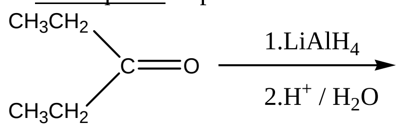
Microanalytical results:	C 54.50%	H 9.17%	O 36.33%
MS (m/z):	$[M]^+$ 88		
IR (cm^{-1}) :	2910 (s), 1725 (s)		
^1H NMR δ (ppm):	10.05 (t, 1H), 4.13 (d, 2H),	3.66 (q, 2H),	1.27 (t, 3H)
^{13}C NMR δ(ppm):	185.2, 82.2, 76.0, 18.3		

- Provide the **molecular formula**, **IUPAC name** and a **structural formula** for this compound.
- Explain clearly **how you arrived at the formulae** using all the information provided.
- What **internal reference compound** would you choose for the NMR spectra?
- What **chemical test** could you use to verify the identity of this compound?

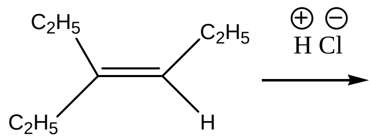
(8 marks)

(b) Predict the **major organic product(s)** from **two** of the following reactions and name the **type of reaction**. (N.B. you are not required to provide a detailed mechanism)

(i)



(ii)



(iii) $CH_3CH_2CH_2—OH + ZnCl_2 \xrightarrow[\text{reflux}]{\text{conc. HCl}}$

(4 marks)

(c) The bromination of propane occurs by a **radical chain mechanism** in the presence of ultraviolet light. In the equation below only the major product is shown.

- Describe in **detail the mechanism** for the formation of this major organic product.
- What would be the other product formed and why is it a minor product?

(4 marks)

Question 5

Timing: you should complete this question in 18 minutes.

(a) In solution simple monosaccharides such as glucose exist predominantly in their cyclised forms.

- Draw a **Haworth projection** of α-D-glucopyranose.
- What do the labels **α-**, **D-** and **pyranose** mean.
- Why is this a **hemiacetal** rather than an **acetal** sugar?

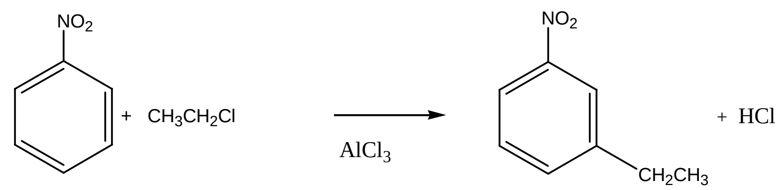
(4 marks)

(b) Draw the structure of (R)-3-chloro-3-methylhexane.

- Provide a **detailed mechanism** for the **S_N1 substitution reaction** between this reagent and sodium methoxide ($NaOCH_3$).
- Provide a **rate law** for this reaction.
- What is a **racemic mixture** and why does it form in this reaction?

(4 marks)

(c) The **Friedyl Crafts alkylation** shown below illustrates a typical reaction of aromatic compounds with electrophilic reagents.



- Provide a **detailed mechanism** for this reaction
- What is the function of the **aluminum trichloride** in the reaction?
- Explain why **substitution** occurs primarily at the **meta** position rather than at the ortho / para positions.

(4 marks)

(d) The **Grignard reaction** between carbon dioxide and ethylmagnesium chloride proceeds as shown below.

$$CO_2 + CH_3CH_2MgCl \xrightarrow[H^+ / H_2O]{} CH_3CH_2C(=O)OH$$

- Provide a **detailed mechanism** for the above reaction
- Provide an **IUPAC name** for the product formed.
- Is this a **nucleophilic** or an **electrophilic** reaction and is it an **addition** or a **substitution** at the carbonyl group, justify your answer.

(5 marks)

EQUATION LIST

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\ln p = \frac{-\Delta H}{RT} + \text{constant}$$

$$\ell n\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$p_i = p_i^O x_i$

$p_{Total} = \Sigma p_i$

$[i] = K_H p_i$

$p_i = p_T x_i$

$p_i = (\%_i / 100) p_{atm}$

$\%_i = ppmv_i \times 10^{-4}$

$K_{sp} = [cation]^c[anion]^d$

$$\frac{m_O}{m_w} = \frac{p_O^o M_O}{p_w^o M_w}$$

$A = \varepsilon l [i]$

1 mole ideal gas = 22.41 dm^3 at STP

$$E = \frac{hc}{\lambda} = h\nu$$

$h = 6.63 \times 10^{-34}$ J s^{-1}

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/k_B T}$$

$k_B = 1.38 \times 10^{-23}$ J K^{-1}

$c = 3.00 \times 10^8$ m s^{-1}

T(K) = T(^{o}C) + 273.15

R = 8.314 J mol^{-1} K^{-1}

1 atm. = 1.013 x 10^5 Pa = 760 torr

TABLE 1

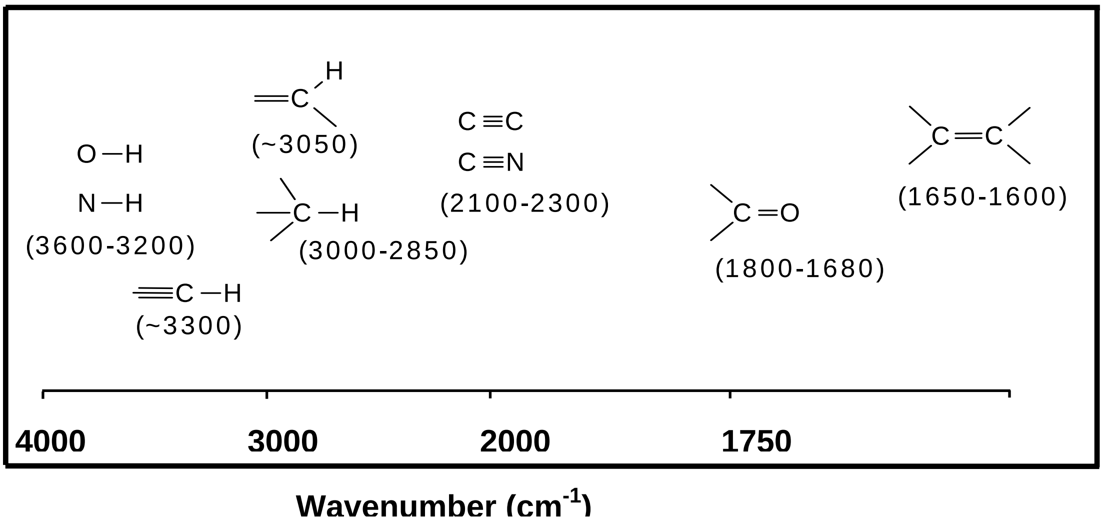
Physical Quantity	Name of Unit	Symbol for Unit
Length	metre	m
Mass	kilogramme	kg
Time	second	s
Electric Current	ampere	a
Thermodynamic Temperature	kelvin	K
Amount of Substance	mole	mol

TABLE 2

Physical Quantity	Name of S.I. Unit	Symbol for S.I. Unit
Volume	cubic metre	m^3
Frequency	hertz	Hz
Velocity	metre per second	ms^{-1}
Acceleration	metre per second squared	ms^{-2}
Density	kilogramme per cubic metre	$kg\ m^{-3}$
Molar Mass	kilogramme per mole	$kg\ mol^{-1}$
Concentration	mole per cubic metre	$mol\ m^{-3}$
Molality	mole per kilogramme	$mol\ kg^{-1}$
Force	newton	N
Pressure	pascal	Pa
Energy	joule	J
Electric Charge	coulomb	C
Electron Potential Difference	volt	V

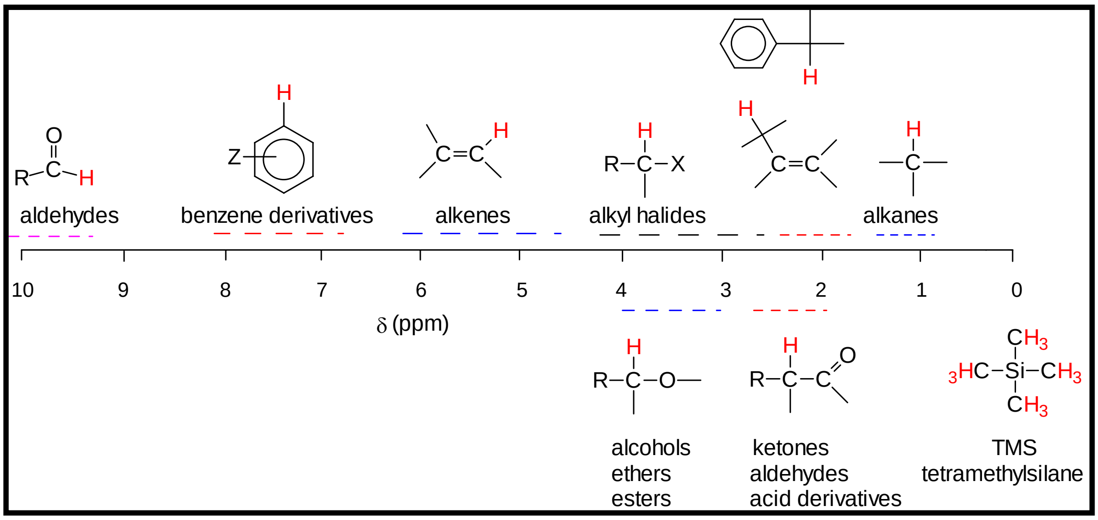
Spectroscopy Tables

Typical Infrared (IR) frequencies of common functional groups

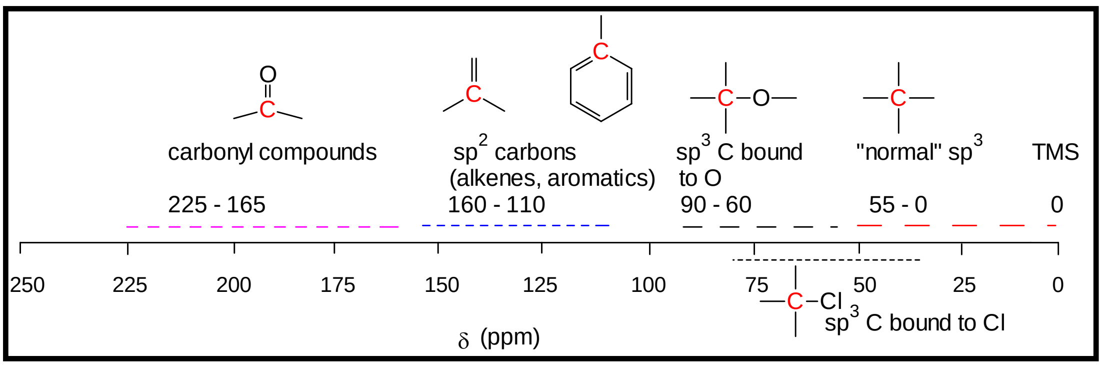


Carbonyl Absorptions ν (cm^{-1}) **Acid chlorides** ~ 1790; **Esters** ~ 1740; **Aldehydes** ~ 1720; **Ketones** ~ 1710; **Acids** ~ 1700; **Amides** ~ 1650

Approximate ^{1}H NMR shifts of protons bound to C in organic compounds



Approximate ^{13}C NMR shifts for groups in organic compounds



PERIODIC TABLE
CH1012:03

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
								1 H 1.008										2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	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
6	55 Cs 132.9	56 Ba 137.3	La- Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	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 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac- Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	. . . .								

s block | *d* block | *p* block

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 146.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	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
Actinide	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 262.1

f block