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SCHOOL OF PHARMACY AND MOLECULAR SCIENCES
Chemistry Department

This paper must be handed in at the end of the Examination: Yes
Release to Library: No

STUDY PERIOD 1 EXAMINATIONS 2006

Cairns Campus

STUDENT NAME:
(*block letters*)

STUDENT NUMBER:

SUBJECT CODE: CH1012:03

SUBJECT NAME: MOLECULAR CHEMISTRY

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

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
Multiple choice scanner sheets Scanner A- E: Yes

MATERIALS STUDENTS MAY USE:
Scientific calculator with no text storage facilities.
Access to an English Dictionary: Yes

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).

1. Are **double bonds** generally stronger or weaker than **single bonds**? Why?

(a) Stronger. There is less electron density between the atoms.
(b) Weaker. There is more electron density between the atoms.
(c) Weaker. There is less electron density between the atoms.
(d) Stronger. There is more electron density between the atoms.
(e) They are both of equal strength.

2. The phenomenon used to differentiate **colloids** and **true solutions** is called the _____ effect.

(a) van't Hoff
(b) Tyndall
(c) Raoult
(d) osmotic
(e) Henry's

3. In the following pairs, Li, Be and Li, Na, which element in each pair will have the greater **metallic character**:

(a) Be, Li
(b) Li, Na
(c) Li, Li
(d) Be, Na

4. Element X reacts with chlorine to form a compound with the formula XCl_2. The oxide of element X is basic. **Element X** is _____.

(a) Rb
(b) Ca
(c) Al
(d) P
(e) H

5. Identify the **polydentate ligand** present and indicate the probable number of **coordination positions** it occupies in $[Ir(dppm)_2Cl_2]^+$.

(a) dppm, 1
(b) Cl^-, 2
(c) Cl_2, 2
(d) dppm, 2

6. Identify the **specific element** that corresponds to the following electron configuration: [Ne]$3s^2 3p^1$

(a) B
(b) Al
(c) Si
(d) C
(e) Ga

7. In molecular liquids, the **attractive intermolecular forces** are _____.

(a) very strong compared with the intramolecular bond energies
(b) strong enough to hold molecules relatively close together to prevent translational
(c) motion
(d) strong enough to keep the molecules confined to vibrating about their fixed lattice points
strong enough to hold molecules relatively close together but not strong enough to keep molecules from moving past each other

8. In **molecular orbital theory**, the bond orders in H_2, H_2^+, and H_2^- are _____, respectively

(a) 1, 0, and 0
(b) 1, ½, and 0
(c) 1, 0, and ½
(d) 1, ½, and ½
(e) 1, 2, and 0

9. What is the molecular formula of **glucose**?

(a) $C_5H_8O_5$
(b) $C_6H_{10}O_6$
(c) $C_4H_{10}O_4$
(d) $C_5H_{10}O_5$
(e) $C_6H_{12}O_6$

10. For a compound to be **aromatic**, how many pi electrons must be in the p_i cloud?

(a) more than the number of sigma electrons
(b) an even number of pairs
(c) an odd number of pairs
(d) an odd number
(e) at least 3 pairs

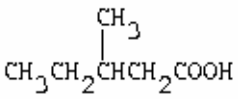
11. In what region of the **IR spectrum** would you find an absorption band that would distinguish between CH_3-C(=O)-OCH_2CH_3 and CH_3-C(=O)-CH_2CH_3?

(a) 1600-1500 cm^{-1}
(b) 1800-1650 cm^{-1}
(c) 3100-2900 cm^{-1}
(d) 3300-3100 cm^{-1}
(e) 1420-1380 cm^{-1}

12. In which **alloy** is the main component copper?

(a) stainless steel
(b) brass
(c) fool's gold
(d) solder
(e) permalloy

13. What is the **IUPAC name** for the following compound?



(a) 3-methylpentanoic acid
(b) 3-isohexanoic acid
(c) 2-ethylbutanoic acid
(d) 2-methylpentanoic acid
(e) 3-ethylbutanoic acid

14. What does **reduction** do to a compound?

(a) It increases the number of carbon-oxygen bonds.
(b) It increases the number of carbon-halogen bonds.
(c) It decreases the number of carbon-hydrogen bonds.
(d) It increases the number of carbon-hydrogen bonds.
(e) a and c

15. Vulcanization works because

(a) sulphur is incorporated into the polymer backbone.
(b) polymer chains are cross-linked by sulphide linkages.
(c) the sulphur removes water from rubber, making it less flexible.
(d) sulphur is attached to the polymer backbone as free thiol groups, and the resulting hydrogen bonding strengthens the polymer.

16. Which metal is **ligated** to a histidine in hemoglobin and myoglobin?

(a) manganese
(b) iron
(c) magnesium
(d) iridium
(e) cobalt

17. What is a general molecular formula for a **cyclic alkene**?

(a) C_nH_{2n}
(b) C_nH_{2n-2}
(c) C_nH_{2n+4}
(d) C_nH_{2n+2}
(e) C_nH_{2n+6}

18. Which of the following compounds will show an **^{1}H NMR spectrum** with 2 doublets, a triplet, and a quartet?

(a) CH_3CH_2-C(=O)-OCH_2CH_3
(b) CH_3CHCl-C(=O)-CH_2-CH(=O)
(c) CH_3-C(=O)-$CH_2CH_2CH_3$
(d) $(CH_3)_2$CH-C(=O)-CH_2CH_3
(e) $CH_3CH_2CH_2$-CH(=O)

19. How many signals would be present in the **^{13}C NMR spectrum** of 2-pentanone?

(a) 3
(b) 6
(c) 4
(d) 5
(e) 7

20. Which of the following compounds is **chiral**?

(a) dichloromethane
(b) difluoromethane
(c) chlorofluoromethane
(d) bromochlorofluoromethane
(e) dibromodichloromethane

21. Which of the following equations is a termination step in the **radical substitution reaction** of methane?

(a) $^{\cdot}CH_3 + Cl\text{-}Cl \rightarrow CH_3Cl + {}^{\cdot}Cl$
(b) $^{\cdot}Cl + {}^{\cdot}CH_3 \rightarrow CH_3Cl$
(c) $Cl\text{-}Cl + h\nu(\text{light}) \rightarrow 2\ {}^{\cdot}Cl$
(d) $\cdot Cl + CH_4 \rightarrow H\text{-}Cl + {}^{\cdot}CH_3$
(e) $^{\cdot}Cl + {}^{\cdot}H \rightarrow HCl$

22. Which statement best describes the mechanism of an **S_N2 reaction**?

(a) back side attack with inversion of configuration
(b) front side attack with inversion of configuration
(c) front side attack with retention of configuration
(d) back side attack with retention of configuration
(e) front side and back side attack with racemization

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 **Group 1A oxides** are **basic** and as a result these elements are termed the Alkali Metals.

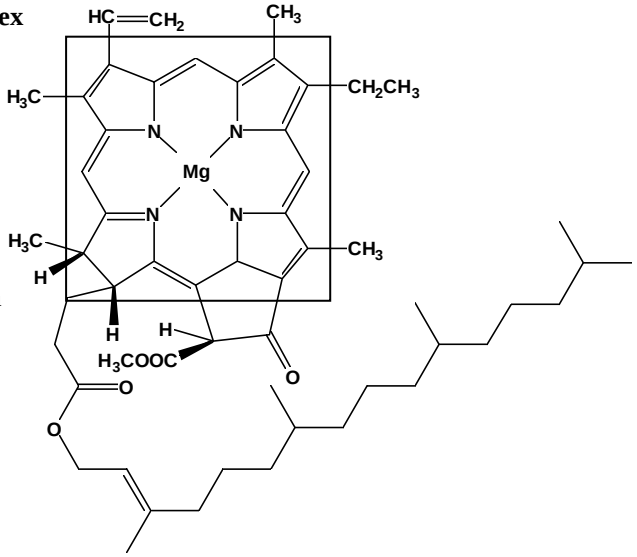
- Explain why the Group 1A oxides are basic using **two different types of oxide**s to illustrate your answer.
- What is an **amphoteric oxide**? Use an example to explain your answer.
- Why is $B(OH)_3$ referred to as **boric acid**?

(6 marks)

Question 2

Timing: you should complete this question in 13 minutes.

(a) Illustrated below is a biological **metal complex** Chlorophyll a.



Chlorophyll a

Using Chlorophyll a as an example illustrate the following :

- **polydentate ligand**
- **coordination number**
- **coordination geometry**
- **chelate effect**
- **conjugation**

Note you only need to draw the section marked inside the square into your answer book.

(6 marks)

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

- $K_3[CoCl_6]$
- $[Mn(phen)_2(H_2O)_2]I_2$ (phen = 1,10-phenanthroline)

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

- sodium dicyanoargentate(III)

(4 marks)

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

- $[Os(NH_3)_4(H_2O)SCN]Cl$

(3 marks)

Question 3

Timing: you should complete this question in 14 minutes.

(a) Explain how the effects of **dispersion forces** are included in the **van der Waals equation**.

- How do **dipole-dipole forces** influence the boiling points of liquids?

(3 marks)

(b) The vapour pressure of *n*-butane is 3.41×10^5 Pa at 30°C and 8.95×10^5 Pa at 70°C.

- Calculate ΔH_{vap} (*n*-butane) in this temperature range.
- Provide a definition for ΔH_{vap} .

(4 marks)

(c) Briefly **describe** the **metallurgical processes** involved in the conversion of magnetite ore (Fe_3O_4) into iron metal.

- Why is iron metal normally transformed into **steel** and how is this process carried out?

(4 marks)

(d) (i) When quantum theory is applied to molecules it is termed **molecular orbital theory**.

- For a single electron in the second shell of a lithium 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 Li_2^+
- Is this molecule likely to be **paramagnetic**? - justify your answer.

(ii) Discuss the following statement with respect to **Band theory** and provide examples to illustrate your answer.:

- the size of the **band gap** is important in determining the conductivity of a solid material.

(4 marks)

Question 4

Timing: you should complete this question in 17 minutes.

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

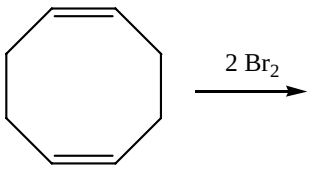
Microanalytical results:	C 35.06%	H 6.62%	Br 58.32%
MS (m/z):	$[M]^+$ 137		
IR (cm^{-1}) :	3000 (s)		
^1H NMR δ (ppm):	3.21 (d, 2H), 1.95 (m, 1H), 1.01 (d, 6H)		

- Provide the **molecular formula**, **IUPAC name** and a **condensed formula** for this compound.
- Explain clearly **how you arrived at the formula** and structure using all the information provided above.
- What peaks would you expect to find in the **^{13}C NMR spectrum** of this compound?
- What **solvent** would you choose for running the NMR spectra?
- How could you convert this compound into the corresponding **alcohol**?

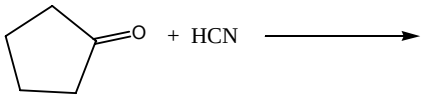
(8 marks)

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

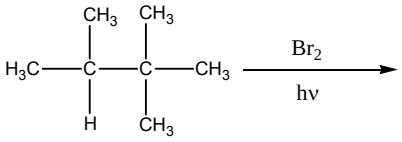
(i)



(ii)



(iii)



(4 marks)

(c) The chlorination of methane occurs by a **radical chain mechanism** in the presence of ultraviolet light, chloromethane is formed along with minor amounts of more highly chlorinated compounds such as dichloromethane, chloroform and carbon tetrachloride.

- Describe in **detail the mechanism** for the formation of chloromethane.
- Draw **3D structures** of chloroform and carbon tetrachloride.
- How would you **purify the mixture** obtained when the reaction is complete?

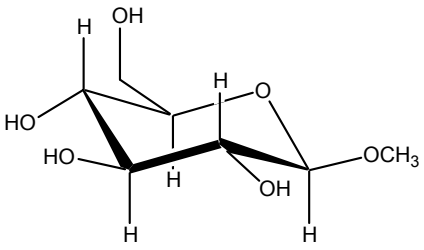
(4 marks)

Question 5

Timing: you should complete this question in 18 minutes.

(a) The following **monosaccharide,** methyl β-D glucoside, is referred to as a **non-reducing sugar**.

- What is a **non-reducing sugar**?
- What is **mutarotation**?
- Will this sugar display mutarotation?



. methyl β-D-glucoside

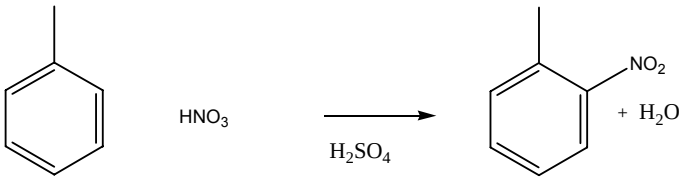
(4 marks)

(b) The **haloalkane** (S)-3-bromoheptane, undergoes nucleophilic substitution as a characteristic reaction.

- Provide a **detailed mechanism** for the **substitution** reaction between this reagent and sodium hydroxide - the solvent system is aqueous methanol.
- Provide a **rate law** for this reaction.
- How would you alter the reaction conditions to bring about the formation of only the ***R* optical isomer**.

(4 marks)

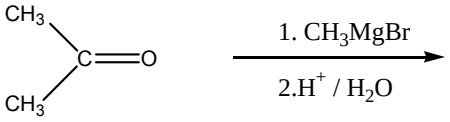
(c) The **nitration** of toluene shown below illustrates a typical reaction of aromatic compounds. Further nitration in this case produces the high explosive 2,4,6-trinitrotoluene (TNT).



- Provide a **detailed mechanism** for this reaction
- What is the **name of the mechanism** and the **IUPAC name** of the product?
- What is the **function of the sulphuric acid** in this reaction?
- Is the methyl group an **activating** group or a **deactivating** group and what does activating / deactivating mean with respect to this type of reaction?

(4 marks)

(d) The **Grignard reaction** between acetone and methylmagnesium bromide results in the formation of an alcohol.



- Provide an **IUPAC name** and draw a **skeletal structure** for the alcohol formed.
- Provide a **detailed mechanism** for the above reaction
- 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

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

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

$T(K) = T(^oC) + 273.15$

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

1 atm. $= 1.013 \times 10^5$ Pa = 760 torr

TABLE 1

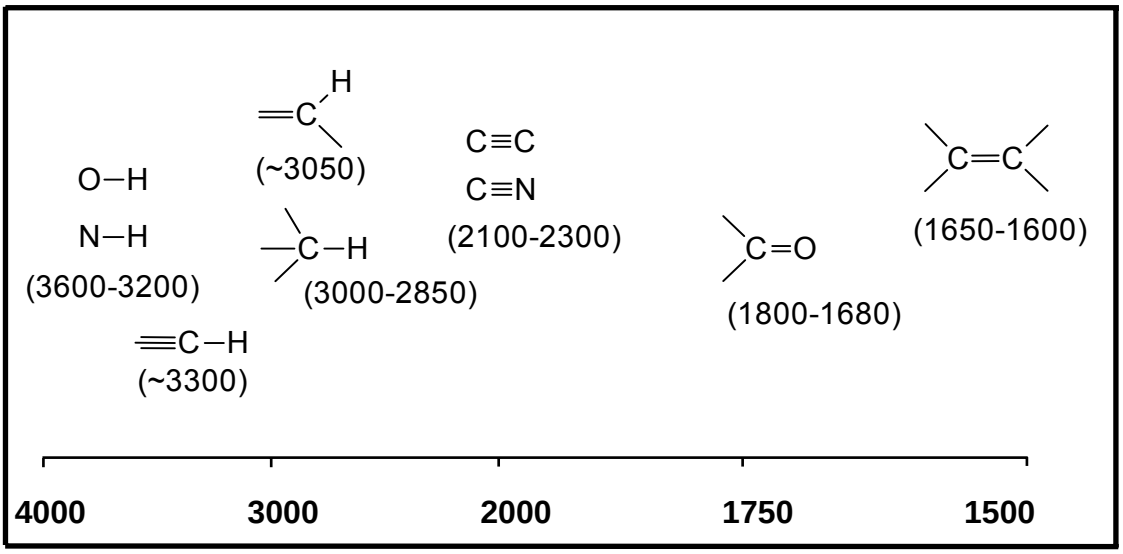
Physical Quantity	Name of Unit	Symbol for Unit
Length	metre	m
Mass	kilogramme	kg
Time	second	s
Electric Current	ampere	a
Thermodynamic Temperature	kelvin	K
Amount of Substance	mole	mol

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

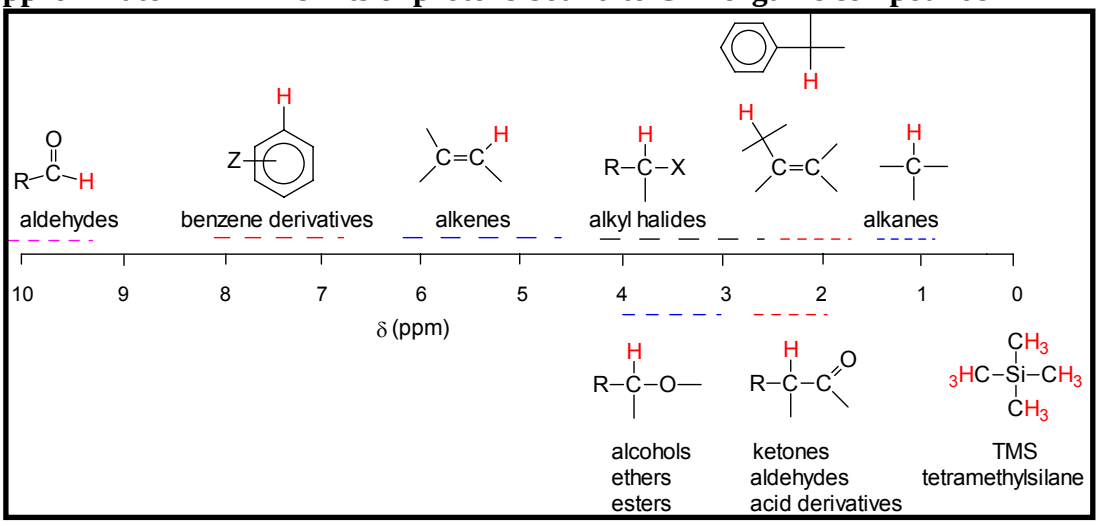
Spectroscopy Tables

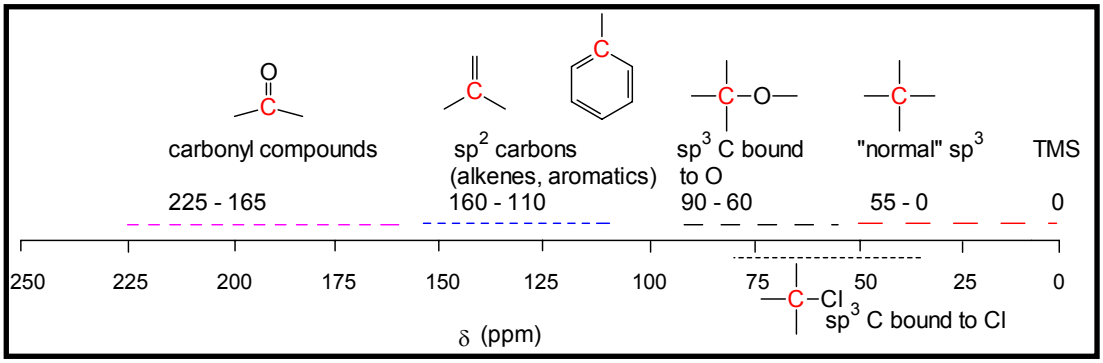
Typical Infrared (IR) frequencies of common functional groups



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