

**OLLSCOIL NA hÉIREANN, GAILLIMH**  
**THE NATIONAL UNIVERSITY OF IRELAND, GALWAY**

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**SUMMER EXAMINATIONS 1999**

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**FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS**

**CHEMISTRY**

*Fourth Paper*

All questions carry 100 marks, distributed as shown where appropriate.

Professor D.J. Cardin  
 Professor R.J. Donovan  
 Professor R.C.F. Jones  
 Professor R.N. Butler  
 and Internal Examiners

Time Allowed: Three Hours

Answer four questions – include at least one question from each Section.  
 No more than two questions from numbers 3, 6 and 9 to be answered.

Use a separate Answer Book for each Section.

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Gas Constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Planck's Constant, $h = 6.626 \times 10^{-34} \text{ J s}$	Velocity of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$
Electronic mass, $m_e = 9.109 \times 10^{-31} \text{ kg}$	Boltzmann constant, $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19} \text{ C}$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$
Faraday constant, $F = 96485 \text{ C mol}^{-1}$	Atmosphere = $101325 \text{ N m}^{-2}$

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## Section A

1. Answer any *two* of the following parts (a), (b) and (c):

(a) Use the equation  $D = \frac{1}{2} \bar{c} \lambda$  to calculate the self diffusion coefficient of  $N_2$  at  $21^\circ C$  and 1 atm pressure; the bond length in nitrogen is 0.370 pm.

[50 marks]

(b) Water is decomposed by electrolysis a KOH solution between two platinum electrodes. The decomposition voltage drop is 1.69V, and the Tafel constants (in volts) are  $a = 0.31$  and  $b = 0.01$  for  $H_2$  evolution at the cathode and  $a = 1.01$  and  $b = 0.059$  for  $O_2$  evolution at the anode. The cathode dimensions are 7 cm  $\times$  7 cm and a current of 0.98 A is flowing through the cell. Neglecting concentration polarisation, compute the electrical energy required to produce one mole of  $H_2$  in this system if the cathode current efficiency can be taken as 100%.

[50 marks]

(c) Calculate the pressure (in  $N\ cm^{-2}$ , Pa and Torr) needed to keep a  $1\ cm^2$  Cu surface "clean" from CO contamination for 1 hr at 300 K, assuming a sticking coefficient of 1, no dissociation of the gas upon adsorption and a surface density of  $1.9 \times 10^{15}$  molecules of Cu/ $cm^2$ . Assume that "clean" means 0.01 of a monolayer in this case.

[50 marks]

2. Answer (a), (b) (c) and (d).

The following data were taken from a shock tube study of the reaction of C atoms with nitric oxide, NO. The C atoms were generated by shock heating gaseous carbon suboxide,  $C_3O_2$ , which is rapidly pyrolysed as:  $C_3O_2 \rightarrow C + 2\ CO$ , and then allowing the C to react with an excess of NO in a pseudo-first order process.

Time / $\mu s$	10	20	30	40	50
[C] / arbitrary	5.74	4.33	3.13	2.33	1.83

(a) Do the data support first order kinetics?

[40 marks]

(b) Calculate the rate constant.

[20 marks]

(c) Why is the study being conducted under pseudo-first order conditions?

[20 marks]

(d) Why is a shock tube being used here?

[20 marks]

3. Write an essay entitled: "*Heterogeneous Equilibria*"

[100 marks]

## Section B

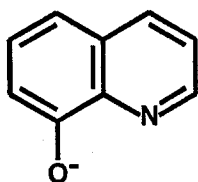
4. *cis*-Cp\*Re(CO)<sub>2</sub>I<sub>2</sub> reacts with one molar equivalent of methyl copper to yield Cp\*Re(CO)<sub>2</sub>(Me)I. Chromatography on alumina afforded two products with identical elemental analyses, A and B. Longer reaction times increased the amount of B present. A and B both exhibit two MC-O stretch bands in their IR spectra (A 2041(vs) and 1966(s) and B 2018(s) and 1954(vs) cm<sup>-1</sup>). The <sup>13</sup>CO NMR spectra of A and B contained 1 and 2 peaks respectively. Reaction of B with *p*-tolylMgBr gave complex C. Photolysis of C in the presence of CO in hydrocarbon solvents gave Cp\*Re(CO)<sub>3</sub>, CH<sub>4</sub> and toluene as products. Photolysis of C in the presence or absence of CO in CCl<sub>4</sub> solution gave CH<sub>3</sub>Cl no *p*-chlorotoluene and a Rhenium complex D. Suggest reasonable formulae and structures for A, B, C and D and mechanisms for the reactions involved. (Cp\* is η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) [100 Marks]

5. Magnetic data for an iron complex FeCl<sub>2</sub>(ox) (see Fig. 1(a) for ligand ox) in the solid state are as follows:

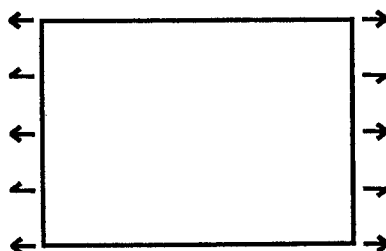
T / K	10 <sup>6</sup> χ <sub>m</sub> (cgsu)	T / K	10 <sup>6</sup> χ <sub>m</sub> (cgsu)
373.2	8242	176.3	10795
343.2	8655	156.9	10899
303.2	9187	137.5	10956
274.2	9563	118.3	10936
234.8	10120	109.1	10882
196.1	10626	88.4	10743

The complex is soluble in acetonitrile and a value of 14335 was measured for 10<sup>6</sup>χ<sub>m</sub> in this solvent at 293 K. Note that μ = 2.83 (χ<sub>m</sub> · T)<sup>1/2</sup>.

The complex crystallised in the space group having the space group diagram shown in Fig.1(b). The volume of the unit cell was 2278 Å<sup>3</sup> and the density was found to be 1.55 g.cm.<sup>-3</sup>.



(a)



(b)

Fig(1)

more on the next page....

**Question 5 continued.**

Provide an equivalent position diagram for the space group and name it

**[30Marks]**

Suggest a possible structure for the complex consistent with all of the data presented and clearly outline the reasons for suggesting this structure. (Note that the limited data do not make it possible to make an unambiguous structural assignment).

**[70 Marks]**

Atomic masses are Fe, 55.85; Cl, 35.45; C, 12.01; N, 14.01; O, 16.0; H, 1.01.  
Avogadro's constant is  $6.022 \times 10^{23} \text{ mole}^{-1}$ .

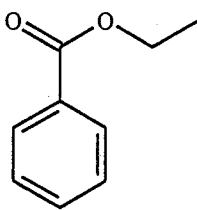
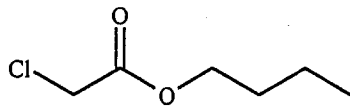
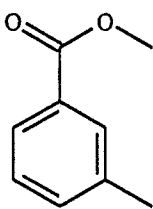
- 6.** Write an essay entitled "The chemistry of silver and gold". **[100 Marks]**

# Section C

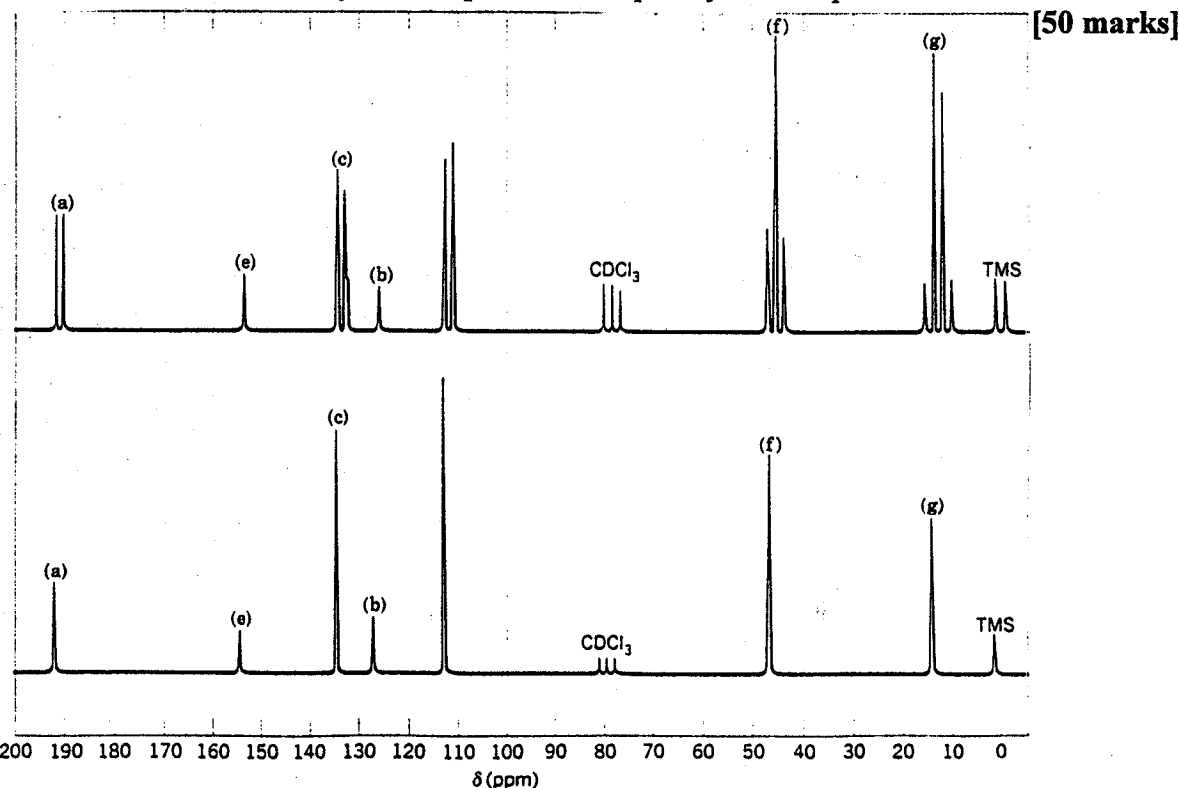
## 7. Answer (a) and (b)

- (a) Compounds containing a carbonyl group often show peaks in their mass spectral data corresponding to a McLafferty rearrangement; with reference to hexan-2-one as a typical ketone, show how this rearrangement may occur and indicate the fragment ions, arising from the rearrangement that you would expect to see in the mass spectrum. [20 marks]

Identify the fragments giving rise to all of the selected peaks in the mass spectrum of each of the following esters. [30 marks]

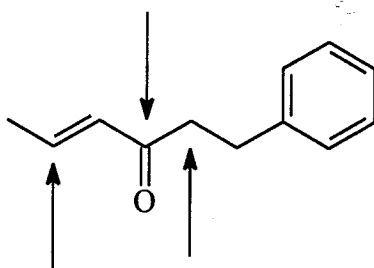
	<p><u>Selected Mass Spectral Data</u></p> <p>150, 122, 105, 77, 51</p>
	<p>79, 77, 57, 56, 51, 49</p>
	<p>150, 119, 91, 65</p>

- (b) A compound (Y) with formula  $C_{11}H_{15}NO$  was isolated from a chemical reaction. Mild air oxidation changed it to a weakly acid compound of formula  $C_{11}H_{15}NO_2$ . The normal and off-resonance decoupled carbon-13 nmr spectra for (Y) are shown. Identify the compound and explain your interpretation of the data. [50 marks]



8. Answer (a) and (b)

- (a) Suggest how an ethyl group might be selectively introduced at the positions indicated in the following molecule (one reaction for each position). Provide a mechanism for each of the reactions and in *one* case suggest how the reaction might be carried out in the laboratory.



[50 marks]

- (b) The protonation equilibria of phenylureas  $\text{XC}_6\text{H}_4\text{NHC(=O)NH}_2$  (A) have been studied in sulphuric acid at 25°C using the equation:

$$\log [\text{AH}^+]/[\text{A}] = -m\text{H}_x + \text{pK}_{\text{AH}^+} \quad (m, \text{H}_x = m_{\text{H}_\text{A}}, \text{H}_\text{A} \text{ and } m_{\text{H}_\text{O}}, \text{H}_\text{O})$$

The results are summarized in the Table:

Sustituent (X)	$m_{\text{H}_\text{A}}$	$-\text{pK}_{\text{AH}^+}$	$m_{\text{H}_\text{O}}$	$\sigma$
4-Cl	0.95	1.48	0.68	+0.373
H	0.94	1.30	0.67	0
3-Me	0.99	1.18	0.77	-0.069
4-Me	0.98	1.22	0.77	-0.17
4-OEt	0.80	1.15	0.65	-0.24

Answer the following:

- (i) which acidity function  $\text{H}_\text{A}$  or  $\text{H}_\text{O}$  is the most appropriate to use and why? [20 marks]
- (ii) The phenylureas have several basic sites (two nitrogens and one oxygen). Do a rough Hammett plot using the  $\text{pK}_{\text{AH}^+}$  values and the Hammett  $\sigma$  values to get an approximate  $\rho$  value for the protonation. Where do you think protonation is occurring? [30 marks]

9. Write an essay entitled "Carbenes: Structure, Formation and Reactions".

[100 marks]