GX304

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2000

FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY AND APPLIED CHEMISTRY (DENOMINATED)

Fourth Paper CH402

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.

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

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°C and 1atm pressure; the bond length in nitrogen is 0.370 nm.

[50 marks]

(b) What is the least negative potential which must be applied to a copper cathode immersed in 0.35M $CuSO_4$ at 298K in order to deposit copper from solution at a current density of 51.7 A m^{-2} ? Assume that concentration polarisation can be neglected. The equilibrium exchange current density (i_0) is 0.20 A m^{-2} and the transfer coefficient (α) is 0.46. E^0 Cu^{2+}/Cu = 0.34V

[50 marks]

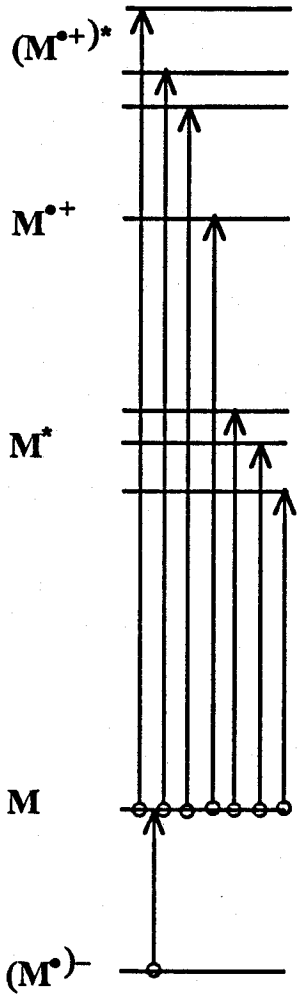
(c) Explain briefly why pulsed voltammetric techniques (normal pulse and differential pulse voltammetry for example) are more sensitive than linear sweep voltammetry.

If a peak current density of 0.221 mA cm^{-2} was measured at 25°C in a linear sweep voltammetric experiment in which the potential was scanned at 100 mV s^{-1}, for an electrochemically reversible one-electron redox transition of a species with a diffusion co-efficient in the electrolyte of 6.76×10^{-6} cm^2 s^{-1}, what is the concentration, in mol dm^{-3}, of the electroactive species in the electrolyte?

[50 marks]

2. The diagram below shows some electronic energy levels for a typical molecule.

Which spectroscopic techniques would be appropriate and what kind of information could you deduce from the transitions indicated?



[100 marks]

3. Describe some of the major problems associated with the use of stainless steels, as materials of construction in the chemical process industries.

[100 marks]

Section B

4. Bubbling hydrogen gas through a pentane solution of $Os(\eta^5\text{-}C_5H_5)Cl(PPr^i_3)_2$, **A**, leads to the formation of a white solid **B**. **B** is a mixture of two isomers, **B(1)** and **B(2)**, the ratio of which is solvent dependent, changing from 20:1 in dichloromethane-d_2 to 9:2 in toluene-d_8. The ^{1}H NMR spectrum of **B(1)** shows a 2H doublet at -10.09 ppm. The ^{1}H NMR spectrum of **B(2)** has a similar pattern with more complex resonances integrating to 2H in the range -7.5 to -15.04 ppm. Treatment of the **B(1)/B(2)** mixture with $NaBH_4$ yields a colourless oil **C** which has a lower P:Os ratio than **B**. When the ^{31}P decoupled ^{1}H NMR spectrum of **C** is observed between -14 and -16 ppm the singlet at -14.6 ppm observed at room temperature collapses as the temperature is reduced and resolves again at the low temperature limit yielding two resonances at -14 and -15 in the ratio of 1:2. Treatment of **A** with HBF_4 yields an ionic red solid **D**. The ^{1}H NMR spectrum of **D** contains a resonance integrating to 1H at -14.36 ppm. **B**, **C** and **D** all show resonances for the C_5H_5 and PPr_3 ligands in addition to those mentioned above. Give reasonable structures for **B(1)**, **B(2)**, **C** and **D** and explain your conclusions.

[100 marks]

5. When a solution of $[Rh(CO)(Cl)(PMe_3)_2]$ (**1**) was exposed to 3 atm of H_2, a series of reactions occurred to give **2** and (**3**+**4**) as outlined in the reaction scheme below. Apart from the normal proton resonances arising from the phosphine ligands, compounds **2** and **3** had ^{1}H absorption at ca. -17 ppm. When the reaction was monitored by infra-red spectroscopy, it was found that ν(MC-O) went from 1905 cm^{-1} to 1920 cm^{-1} to 2150 cm^{-1}.

(a) Draw a reaction scheme outlining the course of the reactions and identifying **2**, **3** and **4**. Your scheme should show the correct structures for **2** and **3**.

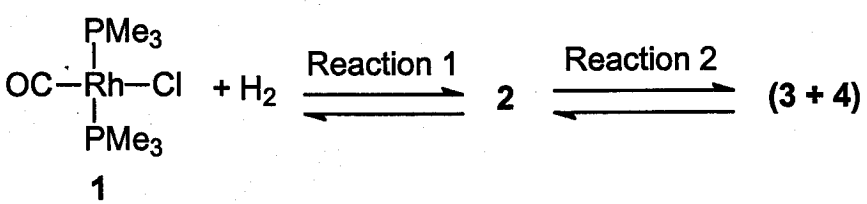
(b) Deduce the oxidation states of the Rh in **1**, **2** and **3**.

(c) What type of mechanism is involved in the reaction of **1** with H_2? Give the reasoning for your answer.

(d) How would you confirm the nature of the mechanism in Reaction 1?

(e) Account for the changes in ν(MC-O) as the reaction proceeds.

(f) What would happen if an excess of PMe_3 were added to **1**?



1

[100 marks]

more on the next page....

6. Answer **(a)**, **(b)** and **(c)**.

(a) Briefly outline the various ways in which crystal defects may be classified. **[10 marks]**

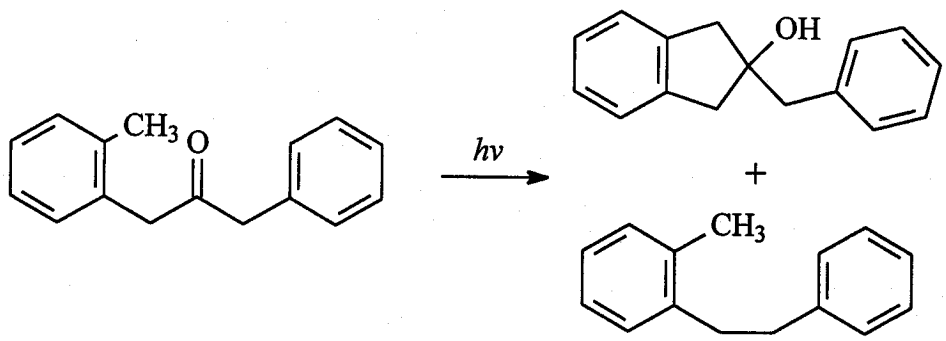
(b) Explain clearly how conductivity measurements are used to determine enthalpies of formation of Schottky and Frenkel defects. **[45 marks]**

(c) Outline in detail the chemistry involved in black and white photography, clearly identifying the role of point defects in this chemistry. **[45 marks]**

Section C

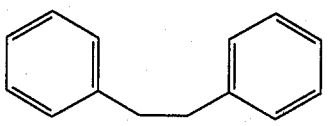
7. Answer all parts

(i) Suggest a mechanism by which the products of the following reaction might be formed:



[25 marks]

(ii) Bibenzyl (A) is also formed in small amounts. Suggest a mechanism by which it might be formed and, in view of the formation of (A), indicate what other aromatic hydrocarbon might be expected.

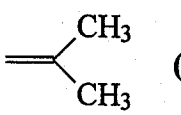
(A) 

[25 marks]

(iii) Explain how the reaction could be carried out experimentally, describing in particular a suitable photochemical reactor.

[25 marks]

(iv) Which type of excited state ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) would you expect to be involved in the formation of the cyclopentanol product in Part (i)? Explain why the observed behaviour might be anticipated for this excited state and draw the structure of the products that might be expected were the ketone to be irradiated in the presence of the alkene (B).



(B)

[25 marks]

8. Answer <u>any two</u> of the following:

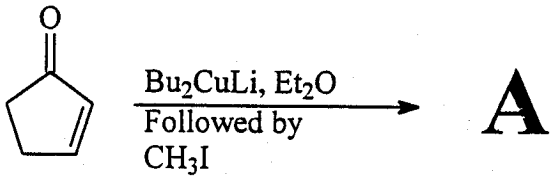
(i) Describe how diethylcopper lithium may be prepared in the laboratory and briefly discuss its reactions with both alkyl and aryl iodides and cyclic epoxides, such as cyclopentene-oxide (shown below). Include the stereochemistry of the reactions and products where appropriate.

[30 marks]

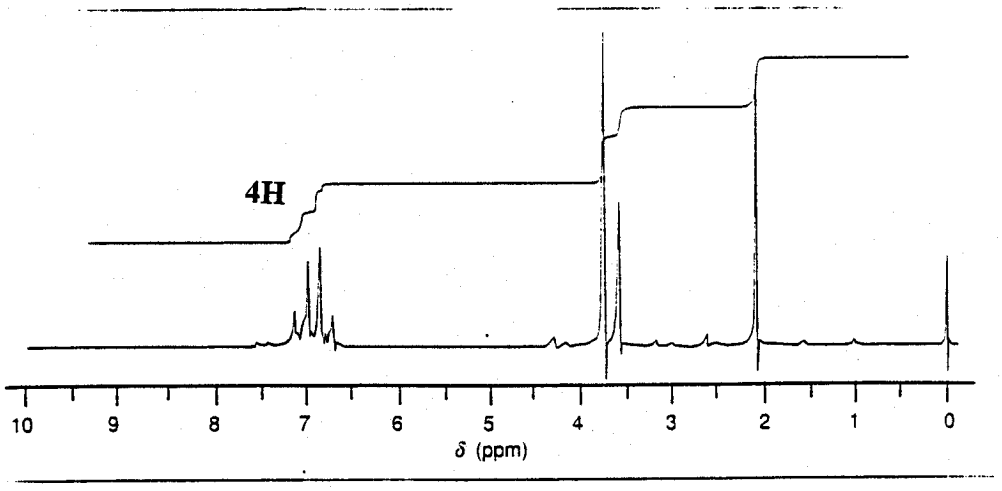
Cyclopentene-oxide

Deduce the structure of **A** and account for its formation and relative stereochemistry.

[20 marks]



(ii) A compound of formula $C_{10}H_{12}O_2$, was isolated from a chemical reaction. Its i.r. spectrum showed an intense absorption at $1720cm^{-1}$. Its ^1H NMR spectrum is shown. Identify the compound and <u>explain your reasoning</u>. **[50 Marks]**



(iii) The 'quaternary ammonium' catalysed S_N2 reaction shown gave good clean second order kinetics i.e. first order in alkyl bromide and first order in aryloxide ion.

$$CH_3CH_2CH_2CH_2CH_2Br + ArO^- \longrightarrow CH_3CH_2CH_2CH_2CH_2OAr + Br^-$$

The main channel of the reaction was as shown but some elimination product $CH_3CH_2CH_2CH = CH_2$ was also formed. Describe the experiments that you would design to try to find out whether the reaction is a true phase transfer (PT) catalysed process or simply a micellar/interfacial type of process. **[50 Marks]**

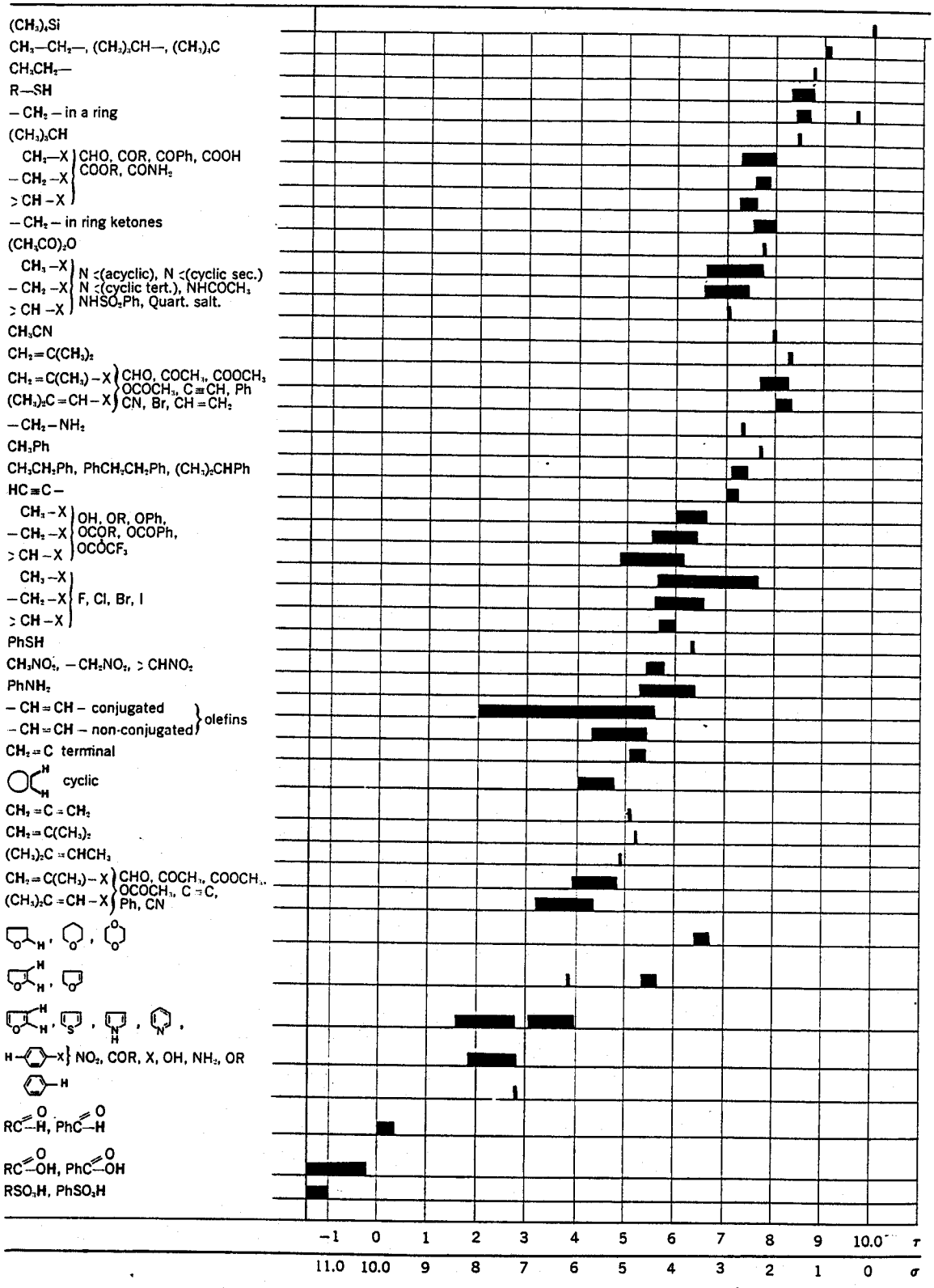
9. Explain how detergents and soaps work.
Classify the four main types of detergents with examples of each and indicate the relative importance of each type in the marketplace.

[60 Marks]

Explain the role of detergent "Builders".
What is the disadvantage of sodium tripolyphosphate, $Na_5P_3O_{10}$ as a washing powder additive?

[40 Marks]

Characteristic NMR Spectral Positions for Hydrogen in Organic Structures



This table is useful for quick qualitative determination of proton spectrum lines by providing a tabulation of line positions obtained using tetramethylsilane as an internal reference. The listing has been kept as simple as possible for this purpose. The proton spectrum lines are arranged according to the chemical shift relative to tetramethylsilane and are given in values of τ and σ. The purpose of this table is to supplement tables available in standard references and to summarize information available in the literature.