

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – MAY 2014, for Internal Students of the
Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

ADVANCED CHEMISTRY THEORY IIIB

Paper 2

Friday 09th May 2014, 09:30-11:45

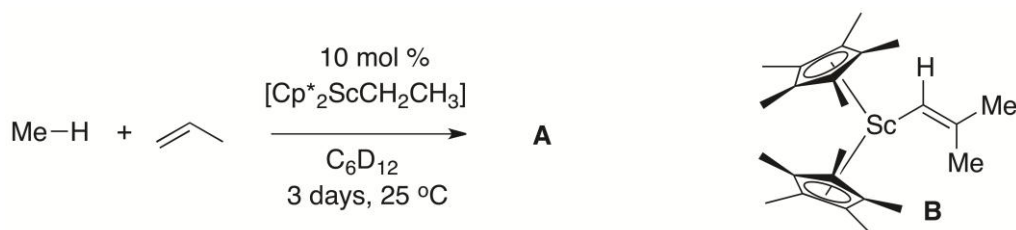
**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

3.I7 – Lanthanides and Actinides

Answer parts a) to c) and **EITHER** part d) **OR** e) of this question.

- Discuss the methods used to separate Ln^{3+} ions from one another ($\text{Ln} = \text{La} - \text{Lu}$).
(5 marks)
- Using the Russell-Saunders coupling and Landé formula, determine the ground-state term symbol and the theoretical magnetic moment of Nd^{3+} .
(6 marks)
- Explain why, in contrast to transition metal complexes, examples of stereoisomerism of lanthanide complexes in solution are rare.
(4 marks)
- The rare-earth metal complex $[(\text{Cp}^*)_2\text{ScCH}_2\text{CH}_3]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) was recently reported to catalyse a reaction between methane and propene.

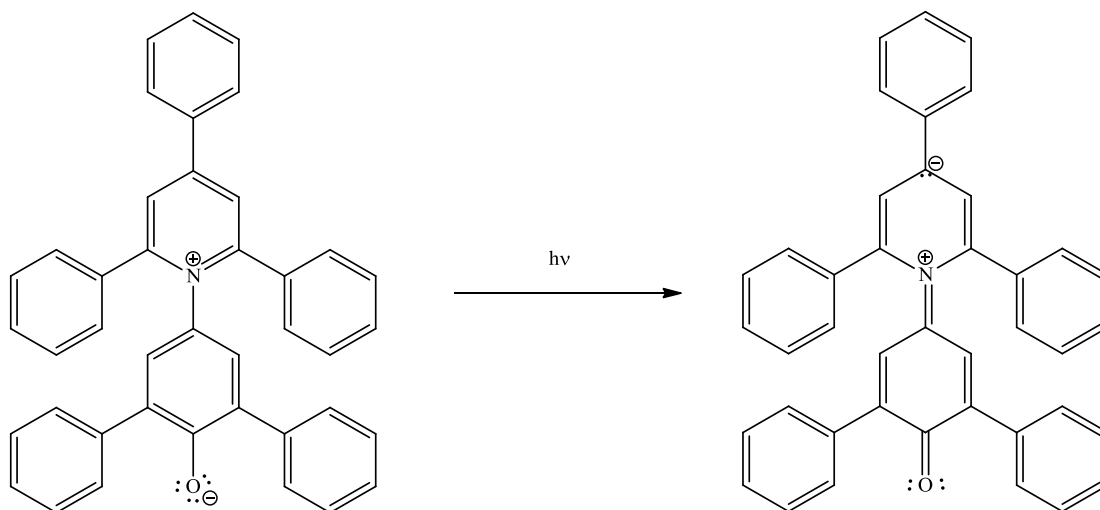


- State the major product of this reaction **A**.
(2 marks)
 - Considering both intermediates and transition states, suggest a reasonable mechanism for the formation of **A**.
(5 marks)
 - Rationalise the formation of the observed organometallic by-product **B**.
(3 marks)
- Uranocene is a sandwich complex with the formula $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}]$.
 - Suggest a possible method for the synthesis of uranocene.
(3 marks)
 - With the aid of molecular orbital theory, rationalise the stability of uranocene in comparison to the theoretical zirconium analogue $[(\eta^8\text{-C}_8\text{H}_8)_2\text{Zr}]$.
(7 marks)

3.I8 – Solvents and Solvent Effects

Answer **ALL** parts of this question.

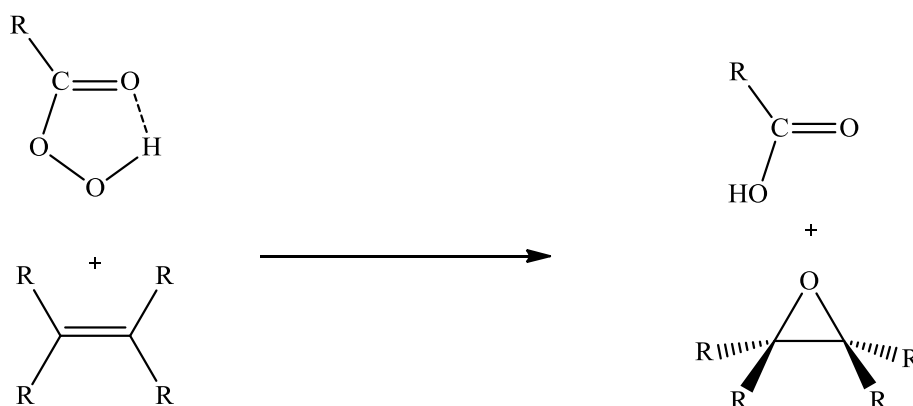
- a) The UV/Vis absorbance band of Reichardt's E_T30 betaine dye shows a very large shift upon moving to more polar solvents.



Explain why this shift occurs and whether more polar solvents will shift the absorbance to higher or lower energy.

(5 marks)

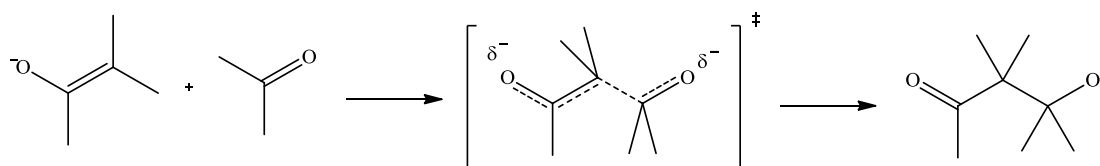
- b) The epoxidation of alkenes with peroxycarboxylic acids gives the corresponding oxirane by an electrophilic 1,1-addition mechanism. This reaction shows a large increase in reaction rate with increasing solvent polarity.



QUESTION CONTINUED OVERLEAF

Answer **ALL** parts below:

- i) Suggest a structure for the transition state for this reaction and explain how this structure fits the observed solvent dependence of the rate of reaction. (3 marks)
 - ii) Explain the increase in rate with increasing solvent polarity using the appropriate reaction free energy diagrams. (6 marks)
 - iii) Explain whether hydrogen-bond accepting solvents will increase or decrease the rate of this reaction. (1 mark)
- c) The aldol addition of enolate ions to carbonyl double bonds gives β -hydroxy aldehydes (aldols) or β -hydroxy ketones (ketols).



Reaction rate data were obtained for this reaction in various solvents as shown in the table below. Also listed are the Kamlet-Taft empirical polarity parameters for each solvent.

Solvent	π^*	k_2 ($\text{s}^{-1} \text{M}^{-1}$)
n-Hexane	0	2.06
Tetrahydrofuran	0.55	5.80×10^{-3}
Acetonitrile	0.66	1.79×10^{-3}
Dichloromethane	0.73	8.48×10^{-4}
DMSO	1.00	

Answer part i) **AND** part ii) and **EITHER** part iii) **OR** part iv) of this question.

- i) Write an equation for an LSER with π^* as the only parameter. Use your LSER to predict the rate of the reaction in DMSO. (4 marks)
- ii) Explain the observed π^* dependence using the Hughes-Ingold Rules. (2 marks)

QUESTION CONTINUED OVERLEAF

- iii) Would the rate of the reaction increase or decrease in solvents with a high α value? Briefly explain your choice, highlighting each of the expected specific interactions and indicating their relative importance to the reaction rate.
(4 marks)
- iv) Would the rate of the reaction increase or decrease in solvents with a high β value? Briefly explain your choice, highlighting each of the expected specific interactions and indicating their relative importance to the reaction rate.
(4 marks)

3.O7 – Polymers

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

Give a brief definition of the following terms:

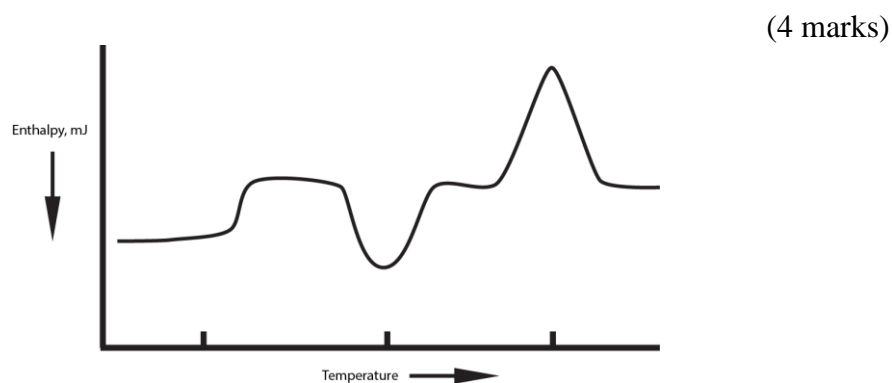
i) plasticisation, paracrystallinity, block copolymer (3 marks)

ii) Highlight the criteria required for the crystallisation of a polymer. What factors determine a high degree of crystallinity? (2 marks)

iii) Under what conditions can the conformation of a polymer chain be described as a “random walk”? (4 marks)

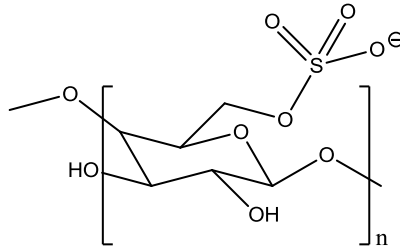
iv) What is Debye-Scherrer broadening? (3 marks)

v) The following thermograph (below) was obtained by DSC of a polymer on heating. Redraw the thermograph and identify the salient features. Draw a similar thermograph on cooling of the same polymer and again identify the salient features observed.



QUESTION CONTINUED OVERLEAF

- vi) For cellulose sulphate (below), explain the effect of the addition of Ca^{2+} has to the polymer. What influence will this have on the T_g ? Give an explanation for your answer.



(3 marks)

- b) Answer **BOTH** parts of this question.

- i) At what point does a growing chain become a polymer? How is this measured and what influence would a crosslinker have on the polymer?

(3 marks)

- ii) What information can a radial distribution function of an amorphous solid tell us? How can this be experimentally verified?

(3 marks)

- c) Answer **BOTH** parts of this question.

- i) Explain the fundamental differences between amorphous and crystalline materials. Give one experimental method that can be used to distinguish between them.

(3 marks)

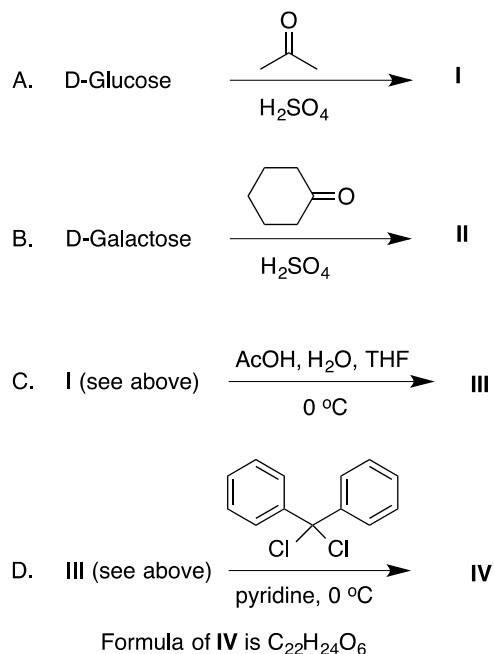
- ii) How does chain length of a polymer affect glass transition temperature? Draw a graph to illustrate your answer.

(3 marks)

3.08 – Carbohydrate Chemistry

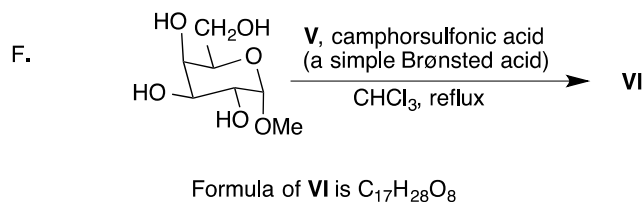
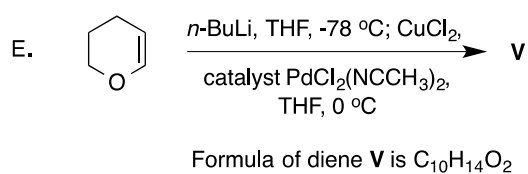
Answer part a) and **EITHER** part b) **OR** part c) of this question.

- a) Suggest structures for the products **I**, **II**, **III** and **IV** formed in all four transformations:



(4 marks each)

- b) Suggest structures for the products **V** and **VI** formed in the following sequence of transformations:

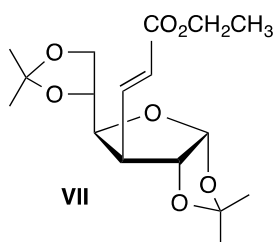


Hint: the final compound **VI** is a diol

(9 marks)

QUESTION CONTINUED OVERLEAF

- c) Suggest a method for the conversion of (D)-glucose into the branched aldose derivative **VII** and comment on the mechanism of the key carbon-carbon bond forming reaction.



(9 marks)

3.P7 – Lyotropics

Answer any **TWO** of the three parts a), b) and c) of this question.

a) Answer **ALL** parts of this question.

The free energy of formation of micelles from monomers may be described by the following expression:

$$(\mu_{mic,m}^{\circ} - \mu_w^{\circ}) = RT \ln x_w - \frac{RT}{m} \ln \left(\frac{x_m}{m} \right)$$

- i) Define m , x_w and x_m .
(1.5 marks)
- ii) What assumption was made in deriving this expression?
(1 mark)
- iii) What is the limiting value of the free energy of formation, as m tends to infinity?
(1.5 marks)
- iv) Hence estimate the critical micelle concentration at 298 K if the free energy of formation has a value of -25 kJ mol^{-1} .
(3.5 marks)
- v) How is the total monomer mole fraction x_{total} related to x_w and x_m ?
(1 mark)
- vi) Hence rearrange the above expression to give an equation for x_{total} in terms of x_m .
(4 marks)

b) Answer **ALL** parts of this question.

- i) Explain what the *neutral* surface of a lipid monolayer is, and describe approximately where it is located.
(2 marks)
- ii) Sketch the form of the lateral pressure profile $p(z)$ across a symmetrical fluid lipid bilayer, identifying each distinct region of the profile.
(2 marks)
- iii) Describe how the profile will change if the hydrostatic pressure is suddenly increased, and how the lipid bilayer will respond to the change.
(2.5 marks)

QUESTION CONTINUED OVERLEAF

- iv) Prove the following relationship between the Gaussian curvature elastic modulus for a monolayer κ_G^m , and that for a bilayer κ_G^b :

$$\kappa_G^b = 2(\kappa_G^m - 2\kappa^m H_o^m t)$$

where t is the distance from the bilayer mid-plane to the neutral surface.

Note: the Gaussian modulus is defined by:

$$\kappa_G = -\int p(z)z^2 dz$$

and you will also need the following relation:

$$\kappa H_o = \int p(z)z dz$$

(6 marks)

- c) Answer **ALL** parts of this question.

The Helfrich equation for a thin fluid lipid bilayer has the form:

$$g_c = 2\kappa(H - H_o)^2 + \kappa_G K$$

- i) Define each term in this equation. (3 marks)
- ii) Write down equations for H and K . (2 marks)
- iii) How is the bilayer value κ^b related to the monolayer value κ^m ? (1 mark)
- iv) If the value of monolayer H_o^m is non-zero, estimate the curvature energy Δg_c stored in a flat lipid bilayer, explaining any assumptions you have made. (3 marks)
- v) Calculate the total curvature energy G_c for a spherical, symmetric composition bilayer vesicle of radius R by integrating the Helfrich equation over the surface of the vesicle, and comment on the result. (3.5 marks)

3.P10 – Soft Condensed Matter

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question

- i) Sketch the temperature dependence of the entropy in a system undergoing a glass transition. Indicate in your sketch both the variation of the entropy with cooling rate and the Kauzmann temperature.

Briefly explain, stating the relevant equations, how the Kauzmann temperature can be used to estimate the viscosity of a glass.

(4 marks)

- ii) State the equations describing the variation of the end-to-end distance of a polymer under a) good solvent conditions, b) the theta condition and c) bad solvent conditions. Briefly explain how the conformation of the polymer changes under these three conditions.

(3 marks)

- iii) Consider the Young's moduli of the following solids:

-Colloidal crystal: 10^{-2} Pa

-Argon: 10^9 Pa

-Silicon: 10^{11} Pa

Estimate the pair interaction energy of the solids in $k_B T$ units, where $T=300$ K.

State what type of interaction is involved in each case.

Data: Diameters: colloid = $0.1 \mu\text{m}$; Argon = Silicon = 0.1 nm .

(3 marks)

- iv) Using the Boltzmann equation show that the entropy of mixing is given by:

$$\Delta S = -nR(x_a \ln x_a + x_b \ln x_b)$$

(5 marks)

QUESTION CONTINUED OVERLEAF

- v) A binary mixture consisting of two components a and b undergoes de-mixing. It is observed that thermal fluctuations promote the formation of small nuclei with a characteristic radius of 1 nm.

Estimate the interfacial tension of the a - b interface.

Using a suitable sketch indicate the region of composition where the de-mixing is likely to occur.

Data: Pair interaction between a - a and b - b : 1 kJ/mol; Density of a and b bulk phases: 6×10^{28} particles/m³

(5 marks)

- b) The Flory-Huggins interaction parameter for a polymer binary mixture with mole fraction composition $x = 0.3$ is $\chi = 0.1$.

Estimate the free energy of mixing.

Is the mixture fully miscible?

(5 marks)

- c) A polymer in solution has an ideal chain length of 160 nm. Upon changing the solvent quality, the polymer stretches to an extension of 20 μm . What force would be needed to maintain the polymer at its ideal end-to-end distance at 300 K?

(5 marks)

3.P12 – Advanced Electrochemistry

Answer part a) and **EITHER** part b) or part c) of this question

At the end of this question you will find a table of Laplace transformations that may be of assistance in answering some parts of this question.

a) Answer **ALL** parts of this question.

- i) Write down the total impedance $Z(s)$ of a resistor R in parallel with a capacitor C .
(2 marks)
- ii) Take $s = i\omega$, $R = 1000 \Omega$ and $C = 0.001 \text{ F}$, and use the result from part i) to draw the Nyquist diagram of the admittance Y for the same circuit. At which value does the plot cross the horizontal axis when extrapolating to $\omega \rightarrow 0$?
(4 marks)
- iii) In Linear Sweep Voltammetry (LSV), the applied potential E is changed linearly with time t , namely $E(t) = E_i + v \cdot t$. E_i is the initial potential and v is the scan rate. Take $E_i = 0 \text{ V}$ and derive an expression for the current-time function $I(t)$ for the parallel RC circuit above. Draw the $I(t)$ curve between 0 and 10 s for $R = 1000 \Omega$, $C = 0.001 \text{ F}$ and $v = 0.1 \text{ V/s}$ and specify the corresponding change in E .

You may want to use the attached table of Laplace transforms for parts of this question.

(9 marks)

b) Answer **ALL** parts of this question.

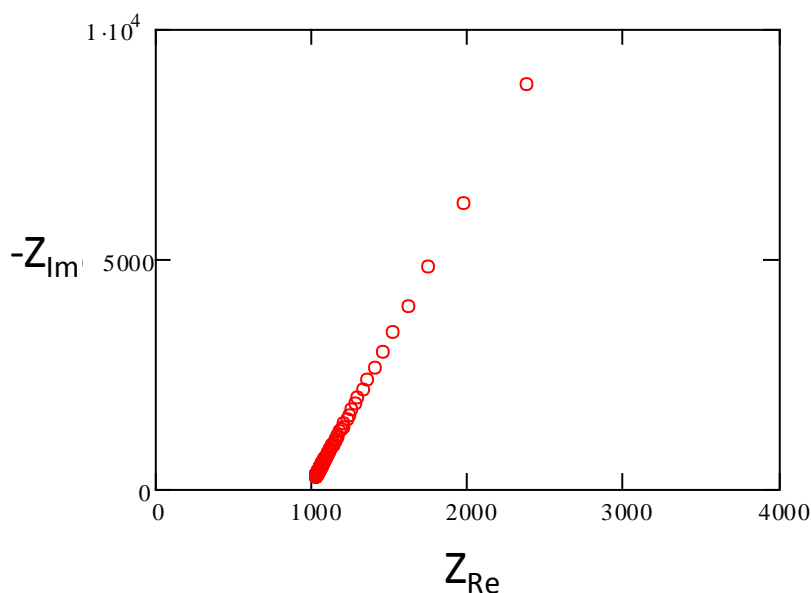
A monolayer of 6-(ferrocenyl)-hexanethiol is formed on a planar gold electrode via the strong Au-S bond.

- i) Draw the cyclic voltammogram (CV), namely the current-potential curve $I(E)$, for such a system in the potential range from -0.2 V to $+0.3 \text{ V}$. Assume that the redox composition of the ferrocene layer is always in accordance with the Nernst equation. Name three pieces of information that can be extracted from such data.
(5 marks)
- ii) How can the same technique be used to determine the interfacial electron transfer rate constant? Which parameter(s) would have to be changed and how does the CV response differ from the case discussed in part i)?
(3 marks)
- iii) How does the CV change if a smaller electrode is used?
(2 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question.

An impedance spectroscopy experiment on a particular electrode gave the following results in the Nyquist plot of the impedance. After extensive polishing of the electrode surface, the data points were found to align almost vertically with the same intercept when extrapolated towards the Z_{Re} axis (data not shown here).



- i) Propose a simple equivalent circuit that could represent the above result. Name all circuit elements used and draw the circuit. (3 marks)
- ii) Suggest an experimental system that is expected to display the impedance behaviour discussed in part i) and justify your choice. (2 marks)
- iii) Write down the expression for the total impedance of the equivalent circuit proposed in part i). Define all terms. In connection with part ii), what is the physical meaning of the intercept when extrapolating the data towards the Z_{Re} axis? To which frequency limit does the intercept correspond? (5 marks)

Additional sheet with common Laplace transforms (from the lecture notes):

$f(t)$	$F(s)$	$f(t)$	$F(s)$
1	$1/s$	$\sinh bt$	$\frac{b}{s^2 - b^2}$
t^n	$\frac{n!}{s^{n+1}}$	$\cosh bt$	$\frac{s}{s^2 - b^2}$
$e^{\alpha t}$	$\frac{1}{s - \alpha}$	$t \sin bt$	$\frac{2bs}{(s^2 + b^2)^2}$
$\sin bt$	$\frac{b}{s^2 + b^2}$	$t \cos bt$	$\frac{s^2 - b^2}{(s^2 + b^2)^2}$
$\cos bt$	$\frac{s}{s^2 + b^2}$	Step function $u(t)$ $f(t) = 1, t \geq 0$ $f(t) = 0, t < 0$	$\frac{1}{s}$
$t^n e^{-\alpha t}$	$\frac{n!}{(s + \alpha)^{n+1}}$	$\delta(t)$	1
$* f(t) e^{-\alpha t}$	$F(s + \alpha)$	$\delta(t - d)$	e^{-sd}