IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2015, 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 1

Thursday 07th May 2015, 09:30-12:30 (maximum)

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

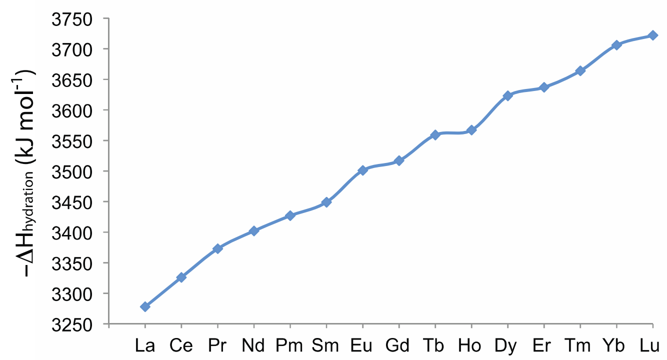
Answer part a), b) and c) and **EITHER** part d) **OR** e) of this question

a) Which lanthanides commonly form dihalides? With use of balanced equations, describe two methods to synthesise lanthanide dihalides.

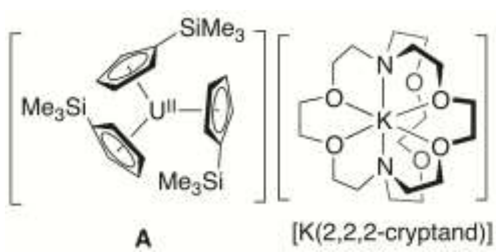
(5 marks)

b) The enthalpies of hydration of Ln^{3+} ions are provided below, identify and explain the trend in these data.

(5 marks)



c) Recently researchers have claimed to synthesize the first organometallic complex containing uranium in the +2 oxidation state. Propose a synthesis of [**A**][K(2,2,2-cryptand)] starting from UCl_4.



(5 marks)

d) Describe the role of relativistic effects in actinide chemistry. Illustrate your answer with an example.

(10 marks)

e) The ground state Gd^{3+} ion has 7 unpaired electrons while that Ho^{3+} has only 4 unpaired electrons. Determine the magnetic moments of these ions (show your working). Using the Russell-Saunders coupling scheme, explain why the magnetic moment of Ho^{3+} is larger than Gd^{3+}.

(10 marks)

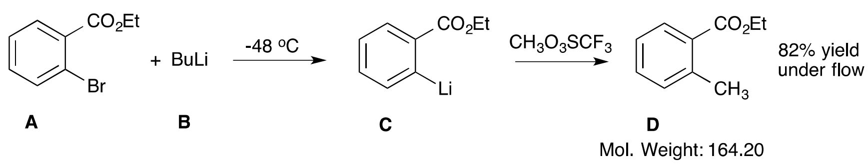
3.I12 – Flow Chemistry

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

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

i) Draw a schematic of a flow reactor that would be suitable for performing the reaction shown below. Discuss why excellent yields of **D** can be obtained under flow conditions while the comparable batch process gives no product at all.

(8 marks)



ii) Using the information in the table below calculate the average residence time, the time it would take to prepare 100 g of product (**D**) and the space-time yield in $g/dm^3/h$.

(4 marks)

Reactor volume	0.2 mL
Concentration of **A**	0.06 mol/dm^3
Flow rate of ***each*** input solution	2.0 mL/min
Yield of **D**	82%

iii) For this particular reaction discuss the challenges that may be encountered for 'scaling-up' this flow process to produce larger quantities of **D**.

(3 marks)

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

i) Discuss the advantages and disadvantages of using PDMS (polydimethyl-siloxane) as a material for fabricating microfluidic flow reactors.

(4 marks)

ii) Describe three 'passive' methods to enhance mixing within microchannels.

(6 marks)

QUESTION CONTINUED OVERLEAF

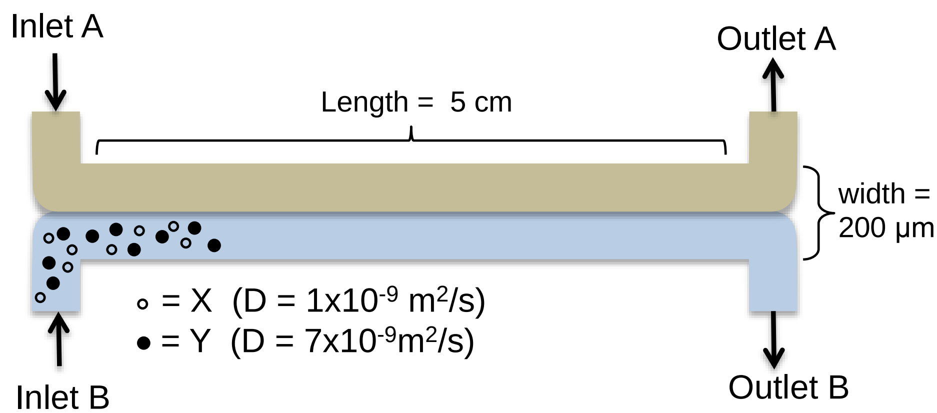
c) Answer **BOTH** parts of this question

i) Explain how the simple flow 'filter' device below can be used to extract **X** from a mixture of **X** and **Y** without the need for a membrane.

(4 marks)

ii) Determine if this device can be used to extract **X** from a mixture of **X** and **Y** infused at inlet B. The channel dimensions of the device are 200 μm wide, 50 μm deep, and 5 cm long. The flow rate at each inlet is 5 μl/min. The molecular diffusion coefficients of **X** and **Y** are 1×10^{-9} m^2/s and $7x10^{-9}m^2/s$ respectively. Show your workings.

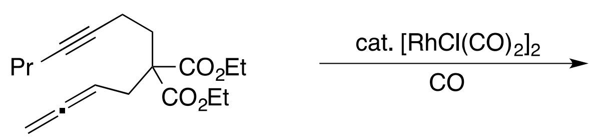
(6 marks)



3.O1 – Organometallic Complexes in Organic Synthesis

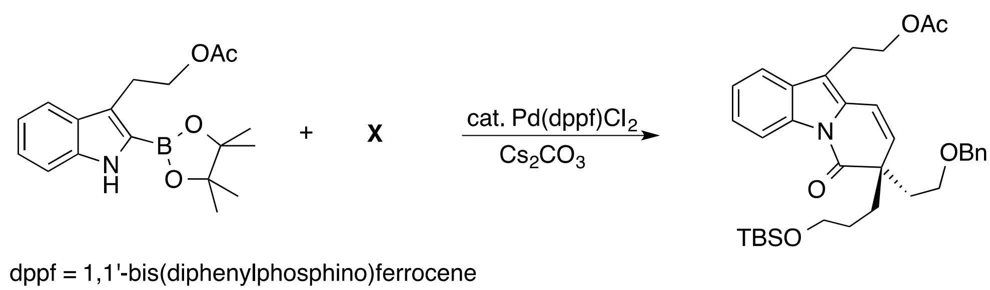
Answer any **FIVE** of the six parts a)-f) of this question.

a) Write down the bicyclo[5.3.0]decadiene product of the following carbonylation reaction.



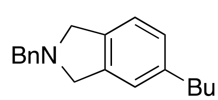
(5 marks)

b) Write down the structure of compound **X** required for the transformation depicted below.



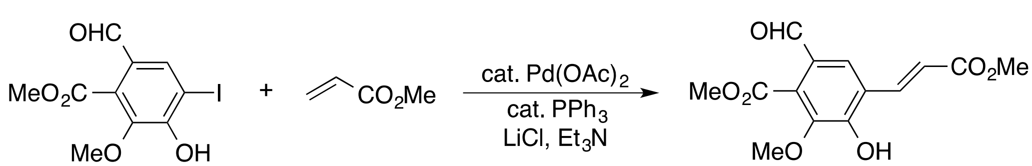
(5 marks)

c) The arene shown below was formed by a [2+2+2] reaction. Write down the two substrates used and suggest a metal catalyst for the reaction.



(5 marks)

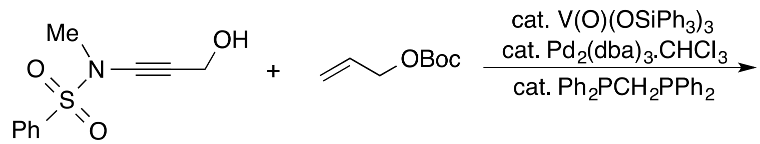
d) Propose a catalytic cycle for the following reaction.



(5 marks)

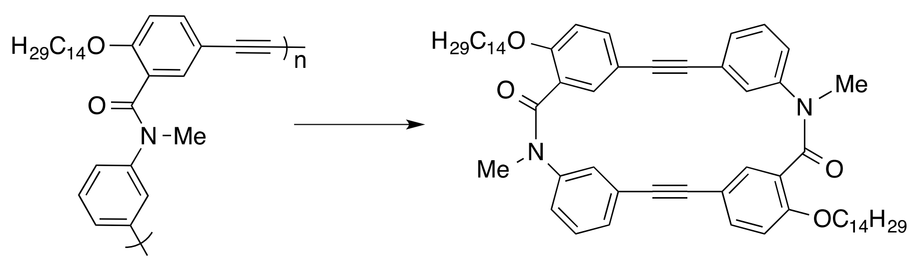
QUESTION CONTINUED OVERLEAF

e) Write down the product of the reaction depicted below.



(5 marks)

f) Suggest a catalyst for the conversion of a polymer into a macrocycle shown below.



(5 marks)

3.O7 – Polymers

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

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

i) Give a brief definition of the following terms:
- anneal
- tacticity
- void volume

(3 marks)

ii) Why does the addition of alumina (as AlO_4) tetrahedra into a silica glass network increase the Tg?

(2 marks)

iii) Explain what Ostwald ripening is. What force drives this process?

(2 marks)

iv) Explain what is meant by radius of gyration.

(2 marks)

v) What is the relationship between molecular weight and Tg? Sketch a graph for this.

(2 marks)

vi) Explain what a Flory or θ solvent is.

(2 marks)

vii) What is free volume?

(2 marks)

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

i) Describe how the glass transition temperature, Tg, may depend upon the Q structure of a glassy silicate polymer? Explain why a glassy, a Q_2 silicate chain, crystallises more rapidly than a Q_4 silicate. Illustrate you answer with examples of each.

(5 marks)

QUESTION CONTINUED OVERLEAF

ii) Explain the factors that cause line broadening in the x-ray diffraction of polymers?

(5 marks)

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

i) What is plasticisation and anti-plasticisation? Give examples of each.

(5 marks)

ii) A commonly used dental polymer, is cured using ultra-violet light. Exposure to the ultra-violet light causes a rapid increase in viscosity, however over exposure causes embrittlement. Explain both of these observations.

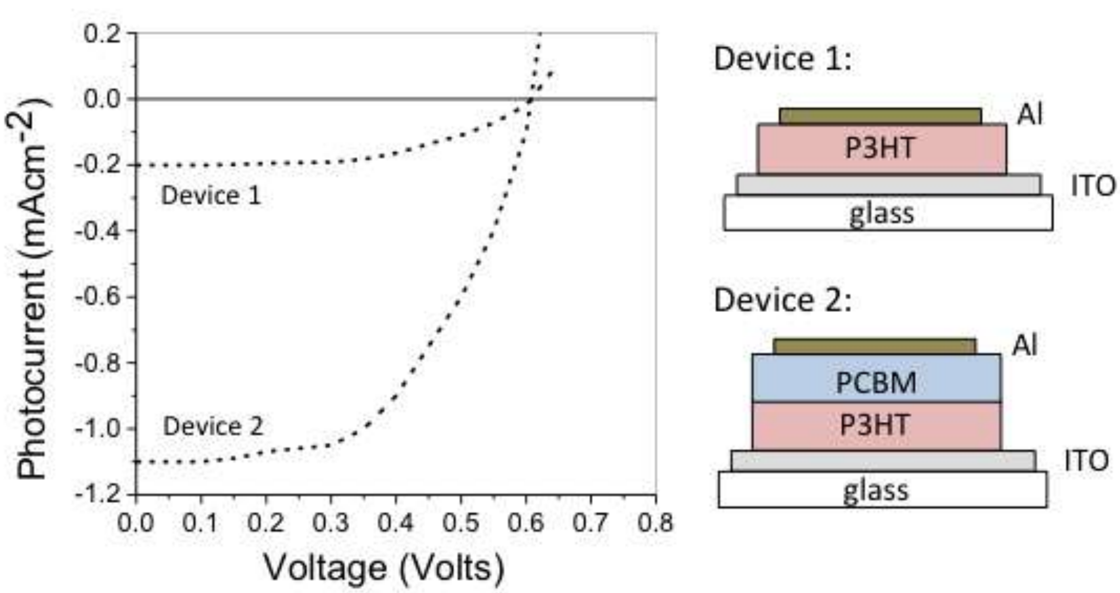
(5 marks)

3.P6 – Molecular Electronic Materials

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

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

The figure below shows the current – voltage characteristics determined for two organic solar cells under simulated solar light (100 Mw cm^{-2}). Device 1 employs single-layer architecture and Device 2 employs a bilayer architecture. The electron affinities of poly-3-hexyl thiophene (P3HT) and fullerene derivative PCBM are 3.2 eV and 4.2 eV, respectively. The ionization potentials for P3HT and PCBM are 5.2 eV and 6.0 eV, respectively. The workfunctions of aluminium and indium tin oxide (ITO) are 4.3 eV and 4.9 eV, respectively.



i) Determine the power conversion efficiency η for Device 2

(3 marks)

ii) Calculate the fill factor FF for Device 2.

(2 marks)

iii) Suggest reasons why Device 2 shows a higher short circuit current than Device 1.

(4 marks)

QUESTION CONTINUED OVERLEAF

iv) Discuss the limitations of the bilayer architecture employed in device 2. Explain how these limitations can be circumvented giving reasons for your answer.

(4 marks)

v) Draw an energy band diagram for device 2 at short circuit in the dark.

(2 marks)

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

An exciton in an organic semiconductor has a radiative rate constant k_r and an emission quantum yield ϕ.

i) Write down an expression for the exciton lifetime τ_f in terms of ϕ and k_r

(2 marks)

ii) State the relationship between the exciton diffusion length L, the exciton lifetime τ_f and the diffusion coefficient D.

(3 marks)

iii) Using the information from parts i) and ii) obtain an estimate of D if the radiative rate constant is 7×10^7 s^{-1} the emission quantum yield is 26% and the diffusion length is 3 nm. Clearly state any assumptions in your calculation.

(5 marks)

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

i) What is a polaron?

(2 marks)

ii) With the aid of suitable diagrams and equations describe the main factors that influence the efficiency (η_{ext}) of an organic light emitting diode.

(8 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) What is the Kauzmann temperature? Briefly explain how it can be used to estimate the relaxation time of a material.

(3 marks)

ii) The preferred end-to-end distance of a polymer strongly depends on the solvent quality. How does the end-to-end distance change with the number of monomers, N, and the solvent quality? Justify your answer using the relevant equations.

(3 marks)

iii) A polymer chain is stretched at 300 K so that its end-to-end distance increases by 300 nm from its ideal value. The applied force is 0.1 pN. Calculate the ideal end-to-end distance of the polymer.

(4 marks)

iv) Use classical nucleation theory to show that the activation free energy for nucleation in a fluid-fluid mixture is proportional to $1/\Delta F_v^2$, where ΔF_v is the cohesive energy.

Further show that the rate of nucleation is proportional to γ^3, where γ is the interfacial tension.

(5 marks)

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

A polymer-polymer mixture can be described using the mean field theory, where the free energy of mixing is given by:

$$\frac{\Delta F_{mix}}{Nk_B T} = \chi x_a x_b + x_a \ln x_a + x_b \ln x_b$$

i) In an experiment it is found that the composition on the spinodal line is $x_a = 0.212$ and $x_a = 0.788$. Calculate the Flory-Huggins parameter at these conditions.

(5 marks)

QUESTION CONTINUED OVERLEAF

ii) Sketch the phase diagram of the binary mixture predicted by the mean field theory given above. Indicate in your diagram the binodal and spinodal lines and critical points, and how these lines/points can be obtained from the free energy.

Further indicate what region in your phase diagram corresponds to spontaneous polymer demixing, i.e., without an activation barrier. Explain what type of structures will emerge during the demixing process in this region.

(5 marks)

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

i) Show that the Young's modulus of a colloidal crystal is given by, $E = k / a$, where k is the curvature of the potential at the equilibrium distance, $r=a$.

(6 marks)

ii) A colloidal crystal is compressed at 300 K by applying a stress equivalent to 10 Pa. The interaction strength at the colloid-colloid equilibrium distance, 10 nm, is 10 k_BT.

Estimate the deformation (tensile strength) of the crystal.

(4 marks)