IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2016, 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 IIIA

Paper 3

Tuesday 03rd May 2016, 14:00-15:30

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) **AND** two parts from b), c), **OR** d) of this question.

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

i) Suggest plausible structures for $[Ln(OH_2)_9]^{3+}$ and $[U(O)_2(OH_2)_5]^{2+}$.

(2 marks)

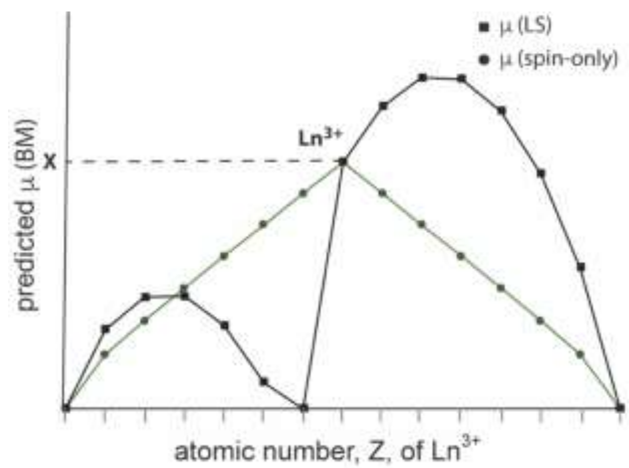
ii) Draw a partial MO diagram for *trans*-$[UO_2]^{2+}$.

(8 marks)

iii) Explain why uranium forms the $[UO_2]^{2+}$ ion whereas lanthanides do not.

(3 marks)

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



With reference to the graph above:

i) Identify for which Ln^{3+} the two plots intercept and explain your reasoning.

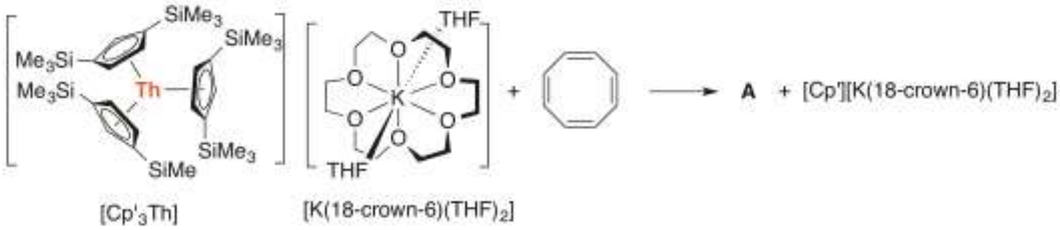
(1 mark)

ii) Show that the value of X is identical, whether it is calculated using the spin-only formula or Landé formula.

(5 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question. A recently discovered reaction is given below:



i) Propose a structure for **A**.

(2 marks)

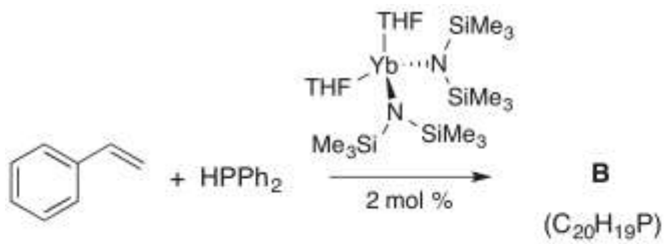
ii) Assign oxidation states to the thorium complexes.

(2 marks)

iii) Rationalise the formation of **A**.

(2 marks)

d) Answer **ALL** parts of this question. A recently discovered catalytic reaction is given below:



i) Propose a structure for **B**.

(2 marks)

ii) Explain the observed regiochemistry of hydrophosphination.

(2 marks)

iii) Suggest why styrene polymerisation is not observed with this catalyst.

(2 marks)

3P3 – Molecular Reaction Dynamics

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

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

i) The following table shows a series of rate constants for electron transfer reactions measured in a photosynthetic reaction centre along with the corresponding edge to edge distances between electron donor and acceptors.

r/nm	**k_{et}/s^{-1}**
0.48	1.58×10^{12}
0.95	3.98×10^{9}
0.96	1.00×10^{9}
1.23	1.58×10^{8}
1.35	3.98×10^{7}
2.24	6.31×10^{1}

Show how you would use the data to determine the value of the electron tunnelling coefficient of the protein environment. Explain all steps and define each symbol used.

(9.5 marks)

ii) State the time-dependent Schroedinger equation in one dimension. Explain all terms.

(1 mark)

iii) Write the time-dependent wavefunction in 1-dimension and compute its square. Comment on your answer.

(2 marks)

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

Derive the Transition State Theory rate of escape from a one-dimensional well. The Hamiltonian of a particle is given by

$H = p^2/2m + V(x)$

where $V(x)$ is a potential well with a minimum at $x=0$ and a barrier with a maximum at $x=x_B > 0$ separating the reactants ($x<x_B$) from the products ($x>x_B$).

i) Sketch the one-dimensional model for this barrier crossing. Label all axes and indicate on the sketch all the characteristic energies and frequencies of the system.

(4 marks)

ii) Derive the transition state rate, k_{TST}. State any assumptions you have made.

(8.5 marks)

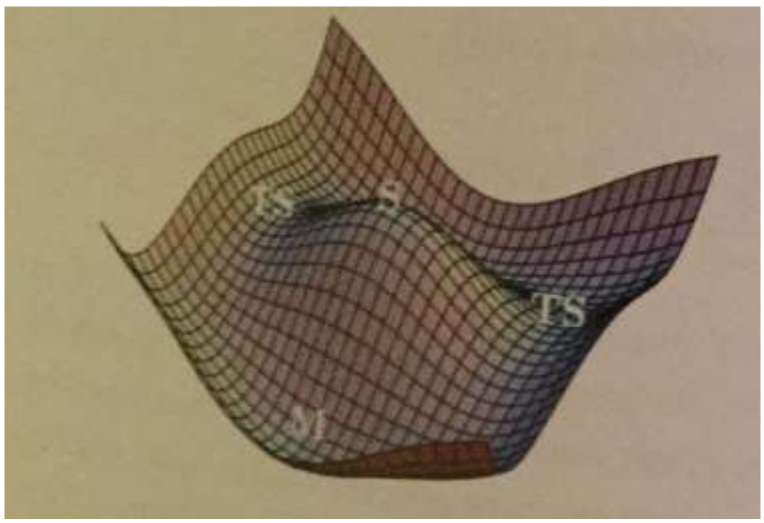
QUESTION CONTINUED OVERLEAF

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

i) Define the Franck-Condon factor and show how to calculate it in a model of two one-dimensional identical harmonic potential surfaces given by $V_1(x) = \frac{1}{2} m\omega^2 x^2$ and $V_2(x) = \frac{1}{2} m\omega^2 (x - \lambda)^2$**,** where m is the mass , ω the frequency and λ a constant**.** Define all symbols used in your equations.

(6.5 marks)

ii) Draw the contour plot that corresponds to the surface plot of the energy landscape below. TS, S and M stand for Transition State, Saddle and Minimum, respectively.



(6 marks)