IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2012, 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

Tuesday 8th May 2012, 09:30-12:30

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.I5 – Bioinorganic Chemistry

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

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

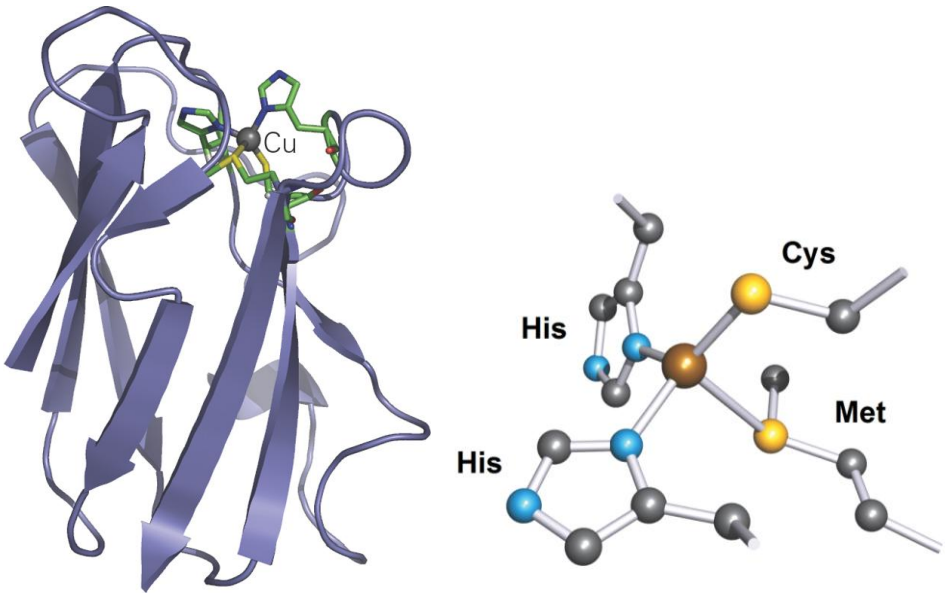
i) Draw the dose-response diagram for an essential element, and give examples of **THREE** essential *trace elements* for humans briefly stating their main biological roles.

(5 marks)

ii) Discuss the role of the entatic state in enzyme catalysis.

(4 marks)

iii) The structure of the blue copper protein *spinach plastocyanin* is shown below, along with a close up of its active site.



With reference to your answer to a) ii) above, discuss how the *spinach plastocyanin* protein is particularly suited for its biological function in electron transfer processes.

(4 marks)

QUESTION CONTINUED OVERLEAF

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

i) What properties of methane make its biological conversion to methanol highly challenging?

(3 marks)

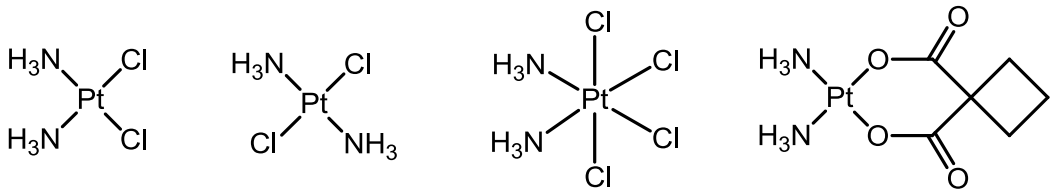
ii) Give a balanced equation for the reaction catalysed by the enzyme methane monooxygenase (MMO).

(2 marks)

iii) Draw the full catalytic cycle for this process showing the oxidation state of the metal centres in each step of the reaction.

(7 marks)

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



i) Draw the equations for the reaction of *cis*-platin (**A**) with excess water.

(3 marks)

ii) Why is this reaction thought to be an important step in the anti-cancer activity of *cis*-platin (**A**)?

(4 marks)

iii) Arrange the platinum complexes **A** to **D** in order of increasing rate of reaction with water. Explain fully your reasoning.

(5 marks)

3.O2 – Biological Chemistry Part 2

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

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

i) When the dye 8-anilinonaphthalene-sulphonic acid (8-ANS) binds to the molten globule state of proteins it shows a large increase in fluorescence emission intensity. Describe how you could use this observation to follow the thermal denaturation of a protein.

(6 marks)

ii) Sketch the expected curve for 8-ANS fluorescence intensity as a function of temperature as the protein is heated through the transition from the native state to the molten globule state and account for the shape of the curve.

(7 marks)

iii) If the protein binds a thermally stable ligand how would you expect this to affect the curve that you drew in part ii)?

(6 marks)

iv) Describe one other, non-spectroscopic, technique that could be used to characterize the thermal denaturation of proteins.

(6 marks)

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

Imagine that a bacterium has been discovered that instead of glucose contains 2-deoxy-2-fluoro-glucose (2-DFG). The bacterium synthesizes two major 2-DFG polymers. One is a linear chain of β-1,4 linked 2-DFG monomer units (polyDFGb) and the second is a branched chain with α-1,4 and α-1,6 linked 2-DFG monomer units (polyDFGa).

i) Based on your knowledge of the different poly(glucose) structures predict possible roles for polyDFGb and polyDFGa explaining your reasoning.

(6 marks)

ii) Assume that the bacteria also contained a protein that could bind to polyDFGb and the binding could be measured by isothermal titration calorimetry. When such a measurement was performed with one protein/polymer pair the following parameters were obtained:

Standard enthalpy of association = + 35.6 kJ mol^{-1}, equilibrium association constant $0.12x10^{5}$ M^{-1} (both measured at 25^{o} C).

Use these values to calculate the thermodynamic contributions to the driving force of the binding reaction and comment on what this tells you about the molecular basis for the protein-carbohydrate interactions.

(7 marks)

QUESTION CONTINUED OVERLEAF

iii) If the DNA of the bacteria turned out to have a very low G:C content and if these bacteria were found to live at low temperature suggest a plausible reason for this observation.

(6 marks)

iv) Assume that the protein that binds polyDFGb described in part ii) of this question regulates the expression of the gene responsible for synthesis of polyDFGb. Suggest a credible model by which this could occur.

(6 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:
- Radius of gyration
- plasticisation
- free volume

(3 marks)

ii) What is Rotational Isomeric State theory? How does it apply to polymers?

(2 marks)

iii) Define the fictive temperature, T_f.

(2 marks)

iv) Describe how neutron scattering can be used to characterise an amorphous solid.

(2 marks)

v) What is a Flory or θ solvent and how does it relate to the conformation of a polymer?

(3 marks)

vi) For an organic polymer how does structure relate to the glass transition temperature, Tg?

(3 marks)

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

i) After addition of a small amount of hydrogen peroxide to poly(propylene) a dramatic increase in Tg is observed. Explain this observation. What experiment could you suggest that would verify your hypothesis?

(5 marks)

ii) Describe how crystallisation occurs in relation to Ostwald ripening. What force drives this process? How does this process relate to the kinetics of crystallisation?

(5 marks)

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

i) Describe what information a radial distribution function of an amorphous solid can tell us. How can this be experimentally verified?

(5 marks)

ii) An inorganic glass is quenched from the melt and afterwards it is annealed. Explain what consequences this might have for the glass structure.

(5 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.

A model surfactant has a hydrocarbon chain volume of $v = 0.25$ nm^3, a full-extended chainlength $l_c = 1.1$ nm, and a preferred headgroup area per molecule of $a_o = 0.6$ nm^2.

i) Define the surfactant packing parameter P.

(2 marks)

ii) Define the term 'cmc'.

(1 mark)

iii) Derive from geometrical arguments the maximum value of P that is compatible with a spherical micelle.

Hint: $V = mv$ and $A = ma_o$, where m is the aggregation number.

(4 marks)

iv) Predict whether the model surfactant will prefer to aggregate into spheres, rods or discs.

(2.5 marks)

v) Estimate the aggregation number m for a cylindrical micelle of diameter $d = 2$ nm and length $L = 10$ nm, formed by a surfactant with a hydrocarbon chain volume of 0.25 nm^3. Assume that the endcaps are hemispheres.

(3 marks)

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

i) 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)

ii) What is the condition for the bilayer to be at its equilibrium area per molecule?

(2 marks)

iii) Describe how the profile will change if the temperature is suddenly increased, and how the lipid bilayer will respond to the change.

(2.5 marks)

QUESTION CONTINUED OVERLEAF

iv) The spontaneous mean curvature H_o of the bilayer is related to the stress profile via:

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

By setting the origin of integration at the centre of the bilayer, deduce the value of H_o for a symmetrical bilayer, explaining your reasoning.

(3 marks)

v) The Gaussian curvature elastic modulus is given by:

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

Referring to your profile p(z) in part i), explain what form of profile would lead to a positive value for κ_G^b of the bilayer. What would be the consequences of this for the lyotropic phase behaviour?

(3 marks)

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

A lipid bilayer vesicle of diameter 5 x 10^{-5} m was aspirated using a micropipette of inner diameter 3 x 10^{-6} m, and the following data were recorded:

Δp / Pa	0	5 x 10^3	1 x 10^4	1.5 x 10^4	2 x 10^4
L_p / m	0	4.1 x 10^{-6}	7.9 x 10^{-6}	1.20 x 10^{-5}	1.61 x 10^{-5}

The data were analyzed using the following equations:

$$\alpha = \left(\frac{A - A_o}{A_o} \right); \; K_A \alpha = \sigma = \frac{\Delta p}{2} \left(\frac{R_p}{1 - R_p / R_s} \right); \qquad \Delta A = 2\pi R_p \left(1 - \frac{R_p}{R_s} \right) L_p$$

i) Define α, K_A, σ and ΔA.

(2 marks)

ii) Calculate and tabulate the values of α, σ, ΔA and K_A, specifying the units in each case.

(8 marks)

iii) Give your best estimate for K_A, explaining your reasoning.

(2.5 marks)