

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 2017, for Internal Students of the
Imperial College of Science, Technology and Medicine**

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

CHEM50003 PHYSICAL CHEMISTRY 2

Tuesday 27th June 2017, 14:00-17:00

**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.**

Q1 – Quantum Mechanics and Photochemistry Part One

Answer **ALL** parts a), b), and c) of this question.

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

- i) For each of the sentences below, state whether it is true or false:
- In a many-electron system, an orbital is an approximate wave function for an electron moving under the influence of the nuclear potential and the average field of all of the other electrons.
 - The rate of Forster energy transfer varies as $1/R^4$ where R is the spatial separation between the donor and the acceptor.
 - A quantum particle on a ring can have zero kinetic energy.
 - In Hückel theory, all overlap integrals are set to 1.
 - The Heisenberg Uncertainty Principle states that the position of a quantum particle cannot be well defined.
 - The ground electronic state of the B_2 molecule is a singlet.
 - For large values of the internuclear separation in H_2^+ , the exchange integral H_{AB} has the value of the overlap integral S_{AB} .
 - Bimolecular photochemistry in solution originates from singlet states.
 - The quantum particle in a box has a well-defined momentum.
 - For a given spatial separation and tunneling coefficient the optimal rate of electron transfer occurs when the free energy ΔG is equal to the reorganization energy λ .
 - In Dirac notation, wavefunctions are said to be normalised if $\langle m | n \rangle = 0$
 - For a diatomic molecule, anharmonicity makes the gradient of the potential energy curve at longer bond lengths away from equilibrium less steep.

(6 marks)

b) The Hamiltonian operator for the Helium atom can be written as:

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2}$$

where m_e is the mass of an electron.

- i) State which term in this Hamiltonian corresponds to the nuclear kinetic energy T_n

(1 mark)

QUESTION CONTINUED OVERLEAF

- ii) Briefly explain the Born-Oppenheimer approximation. What value does T_n take if this is applied to the He atom and why? (3 marks)

- iii) Write out the term in the above Hamiltonian that corresponds to interelectronic repulsion. (1 mark)

The ground state two-electron wavefunction for the He atom can be written as:

$$\Psi(1,2) = \phi(1)\phi(2)$$

where ϕ is a 1s orbital.

- iv) If the interelectronic repulsion term identified in part (iii) was not present, would writing the two-electron wavefunction as an orbital product in this way be an approximation? Briefly explain your answer. (2 marks)
- v) Electrons are indistinguishable fermions, and many-electron wavefunctions are antisymmetric. What happens to such wavefunctions when the coordinates of two indistinguishable particles are swapped? (1 mark)

- vi) Show that a wavefunction of the form

$$\Psi(1,2) = \phi(1)\phi(2)[a(1)b(2) - b(1)a(2)]$$

is antisymmetric. (2 marks)

- vii) Is the wavefunction given in part (vi) for a singlet or a triplet electronic state? (1 mark)
- viii) Briefly explain what a minimal basis set is in molecular orbital theory. For H_2 at its equilibrium geometry, why does such an approximation give an energy higher than the best numerical solution? Briefly outline two ways in which a minimal basis set calculation can be improved. (3 marks)
- ix) Would you expect the bond length of the N_2 molecule to be longer in its first electronic excited state compared to its ground state? Briefly explain your answer. (2 marks)

QUESTION CONTINUED OVERLEAF

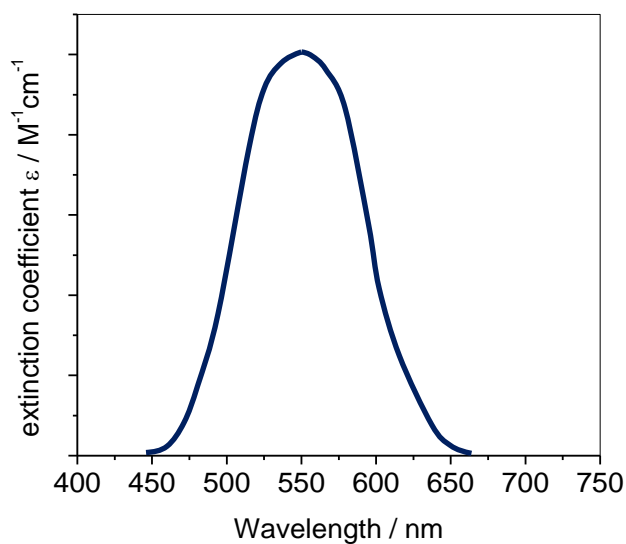
c) Answer **ALL** parts of this question.

i) Draw a Jablonski diagram and clearly indicate on this diagram the following optical transitions:

- $S_0^0 \rightarrow S_1^2$
- $S_1^0 \rightarrow S_0^1$
- $T_1^0 \rightarrow S_0^0$

(3 marks)

ii) Figure 1 below shows an absorption spectrum of a dye molecule. The dye molecule exhibits a peak at 550 nm and a molar extinction coefficient (ϵ) of $80,000 \text{ M}^{-1}\text{cm}^{-1}$ at 550 nm.



Using the Strickler-Berg relationship, estimate the natural radiative rate constant, k_r for this dye molecule. If τ_o is 500 picoseconds for this dye, what is ϕ_f ?

(5 marks)

Q2 - Thermodynamics and Statistical Thermodynamics

Answer **ALL** parts of this question.

- a) The fundamental equation can be written down for the molar quantities G_m , V_m and S_m .
- i) Sketch a graph of G_m (equivalent to chemical potential μ) versus T across the boiling point of a pure liquid, for some initial pressure p_i , and explain the form of the plot and why it arises. (3 marks)
- ii) On the same graph sketch the situation for a higher pressure p_f , explaining the differences between this plot and the plot at the lower pressure p_i and state whether the boiling point goes up or down with increased pressure and why. (2 marks)
- b) Derive the van't Hoff equation by considering the thermodynamic balance between two compartments separated by a semipermeable membrane, one containing solute and one containing solute plus solvent. (6 marks)
- c) The measured enthalpy and entropy of unfolding and change in heat capacity for the protein carbonic anhydrase at 25⁰ C and at pH 4.5 are:

$$\Delta H = 725 \times 10^3 \text{ J mol}^{-1}, \Delta S = 2218 \text{ J K}^{-1} \text{ mol}^{-1}, \\ \Delta C_p = 16.0 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}$$

- i) Calculate the Gibbs energy of unfolding at 25° C and pH 4.5 (2 marks)
- ii) There are two main contributions to the difference in heat capacities of an unfolded and folded protein. One of these is the entropic difference caused by the change in bonding on vibrational frequencies. Describe the other main contribution and briefly discuss how it arises. (2 marks)
- iii) Sketch the relationship between the Gibbs energy of unfolding and temperature for a typical protein. Label all of the salient points and explain, using the graph, why addition of denaturant increases the temperature for the cold-induced unfolding transition and can bring it above the freezing point of water. (3 marks)
- d) What is the fraction of molecules in state 'i' in a system with N molecules at equilibrium with a temperature T (Boltzmann distribution)? Define all terms. (3 marks)

QUESTION CONTINUED OVERLEAF

- e) For the same system define the molecular partition function. If the state 'j' has degeneracy g_j and energy ϵ_j write down the molecular partition function as a sum over energy levels.

(3 marks)

- f) Water has three normal (vibrational) modes with frequencies $\nu = 1595, 3657, 3756 \text{ cm}^{-1}$

- i) Assuming that each vibrational mode can be treated as a simple harmonic oscillator, write down the expression for the vibrational partition function in terms of the mode frequency ν .

(2 marks)

- ii) Calculate the vibrational contribution to the molecular partition function at 298K, and comment on the result.

(6 marks)

- g) Upon folding, the average frequency of the low frequency vibrational modes in the amino acids of the protein chymotrypsin drops from $\nu = 200 \text{ cm}^{-1}$ to 150 cm^{-1} . There are 245 amino acids in chymotrypsin.

- i) Assuming ten low frequency modes per amino acid on average, use statistical thermodynamics to calculate the contribution of changes in vibrational frequency to the entropy and free energy difference between the folded and unfolded forms of chymotrypsin.

(Note that the vibrational contribution to the molar entropy of a molecule is $S_{\text{vib}}(T) = (U(T) - U(0))/T + R \ln q_{\text{vib}}$, and for each mode in the simple harmonic oscillator model $U(T) = N_A h c \nu / (e^{+h c \nu / k T} - 1)$, $U(0) = N_A h c \nu / 2$, where all terms have their usual meaning.)

(6 marks)

- ii) For chymotrypsin at 25°C and pH 4.5:

$$\Delta H = 710 \times 10^3 \text{ J mol}^{-1}, \Delta S = 2573 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p = 12.8 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}$$

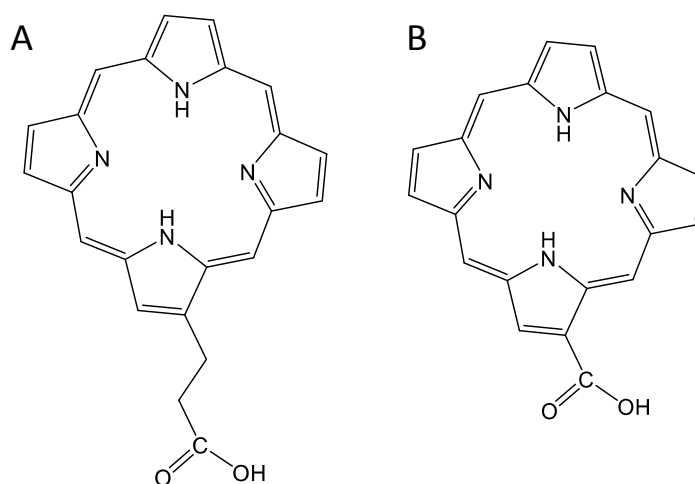
Given your knowledge of the thermodynamics of protein folding and the result of g) part i), comment on the ways in which vibrational entropy contributes to the temperature dependence of the folding process.

(2 marks)

Q3 - Electrochemistry and Photochemistry Part Two

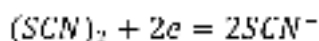
Answer **ALL** parts of this question.

- a) **A** and **B** are dyes synthesized for use in dye sensitized solar cells. Both dyes can bind to TiO_2 via the carboxylate group to form donor-acceptor assemblies namely, **A-TiO₂** and **B-TiO₂**. In both of these donor-acceptor assemblies the porphyrin functions as a light absorber and electron donor and the TiO_2 functions as an electron acceptor. With the aid of a suitable equation and diagram explain how the rates of photoinduced electron transfer would differ in these two donor acceptor assemblies.



(7 marks)

- b) In one type of dye-sensitized solar cell (described in part a)), redox couples comprising pseudohalogens are dissolved in the electrolyte. One such redox couple involves the thiocyanate ion for which the half-cell reaction is:



Typically, the electrolyte contains 25 mM of the oxidised form and 100 mM of the reduced form. If the measured equilibrium potential of a Pt electrode in contact with this electrolyte is 0.18 V, calculate the standard potential of the $(\text{SCN})_2/\text{SCN}^-$ redox couple. (Concentrations may be taken to be equal to activities and the temperature may be assumed to be 25⁰ C).

(9 marks)

QUESTION CONTINUED OVERLEAF

- c) After the dye (described in part (a)) absorbs a photon and donates an electron to the TiO_2 it is regenerated by reaction with one half of the $(\text{SCN})_2/\text{SCN}^-$ redox couple. Write a balanced equation for the reaction between the reduced dye (which you may represent as A^+) and the relevant species from the $(\text{SCN})_2/\text{SCN}^-$ redox couple.
- (4 marks)
- d) The diffusion coefficients of the SCN^- ion and of $(\text{SCN})_2$ are of importance to the operation of the cell, as diffusion is the dominant means of transport in such cells. The values of D have been measured (for the electrolyte composition specified in part (b)) and have been found to be roughly equal in value.
- i) What are the units of the diffusion coefficient? Explain your answer.
- (4 marks)
- ii) Comment on the fact that the diffusion coefficients for SCN^- and $(\text{SCN})_2$ are roughly the same.
- (6 marks)