

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 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 II

Physical Chemistry

Monday 13th June 2016, 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.**

2.P6 – Quantum Chemistry

Answer part a) **AND** either part b) **OR** part c) of this question.

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

i) Quantitatively draw and label Molecular Orbital (MO) diagrams for N_2 and O_2 . Exclude the MOs formed from the IS atomic orbitals. (6 marks)

ii) Explain the origin of the paramagnetism of O_2 ; you may wish to reference your energy diagram from part i). Indicate the rule you are using to determine the occupancy of the MOs. (2 marks)

iii) Below are the Huckel energy levels for the cyclic systems C_6H_6 , C_8H_8 and $C_{10}H_{10}$. Calculate the delocalisation energy for each molecule; remember that the delocalisation energy is relative to the energy of the corresponding number of ethene molecules. (3 marks)

For C_6H_6

$$E_0 = \alpha + 2\beta$$

$$E_1 = \alpha + \beta$$

$$E_2 = \alpha - \beta$$

$$E_3 = \alpha - 2\beta$$

$$E_4 = \alpha - \beta$$

$$E_5 = \alpha + \beta$$

C_8H_8

$$E_0 = \alpha + 2\beta$$

$$E_1 = \alpha + \sqrt{2}\beta$$

$$E_2 = \alpha$$

$$E_3 = \alpha - \sqrt{2}\beta$$

$$E_4 = \alpha - 2\beta$$

$$E_5 = \alpha - \sqrt{2}\beta$$

$$E_6 = \alpha$$

$$E_7 = \alpha + \sqrt{2}\beta$$

$C_{10}H_{10}$

$$E_0 = \alpha + 2\beta$$

$$E_1 = \alpha + 1.62\beta$$

$$E_2 = \alpha + 0.62\beta$$

$$E_3 = \alpha - 0.62\beta$$

$$E_4 = \alpha - 1.62\beta$$

$$E_5 = \alpha - 2\beta$$

$$E_6 = \alpha - 1.62\beta$$

$$E_7 = \alpha - 0.62\beta$$

$$E_8 = \alpha + 0.62\beta$$

$$E_9 = \alpha + 1.62\beta$$

iv) Comment on the relative separations of the MOs in question iii). Indicate whether each molecule is aromatic. (2 marks)

v) Explain why is not possible to solve the Schrodinger wave equation analytically for systems of more than two electrons. (2 marks)

QUESTION CONTINUED OVERLEAF

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

For Cyclobutadiene, C₄H₄

- i) Calculate the Huckel MO energies and draw a labelled energy level diagram and assign the electrons to the orbitals. This type of problem results in a circulant matrix (form of the Huckel determinant) and can be solved by use of the following equations

$$x = -2\cos\left(\frac{2\pi k}{n_c}\right) \text{ where } k = 0, 1, \dots, (n_c-1), \text{ where } n_c \text{ is the number of carbon atoms.}$$

$$E = \alpha - \beta x$$

(6 marks)

- ii) Explain the significance of the two MOs with the same energies

(2 marks)

- iii) Calculate the delocalisation energy

(2 marks)

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

- i) For HeH⁺ write the full Hamiltonian indicating the origin of each term. Assume the use of the Born-Oppenheimer approximation in setting up the Hamiltonian.

(6 marks)

- ii) Draw a quantitative Molecular Orbital diagram for HeH⁺.

(2 marks)

- iii) Explain what properties of matrix determinants are significant in representing wave-functions for molecular orbital calculations

(2 marks)

2.P9 – Photochemistry

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

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

- i) Draw a Jablonski diagram, clearly illustrating on this diagram the processes of light absorption, intersystem crossing, internal vibrational relaxation, internal conversion, fluorescence and phosphorescence. Also indicate on this diagram the $T_1^0 \rightarrow S_0^3$ optical transition.

(7 marks)

- ii) Kinetic measurements were performed on a series of donor-bridge-acceptor molecules to investigate the influence of Gibbs free energy (ΔG) on the rate constant (k_{et}) for photo-induced electron transfer. The length of the covalent bridge was kept constant and ΔG was modulated by varying the chemical structure of the acceptor moiety of the molecule. The results obtained from these investigations are given in Table 1 below.

Table 1:

$\Delta G / \text{eV}$	0.65	0.70	0.75	0.85	0.95	1.00	1.05	1.1
$k_{et} (\times 10^6) / \text{s}^{-1}$	0.73	1.2	1.98	4.19	5.38	5.38	4.19	2.54

Using the data in Table 1, determine the reorganization energy λ . Explain, with the aid of suitable equations and figures, the physical origin of the trend in k_{et} *versus* ΔG observed in this experiment.

(8 marks)

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

- i) Discuss the role of carotenoids in the photo-protection of photosynthesis in plants.

(5 marks)

- ii) A molecular chromophore has a fluorescence lifetime of 8.5 ns and a fluorescence quantum yield of 0.3. Assuming a full width half maximum for the $S_0 \rightarrow S_1$ absorption transition of 1000 cm^{-1} , estimate the peak extinction coefficient of the transition.

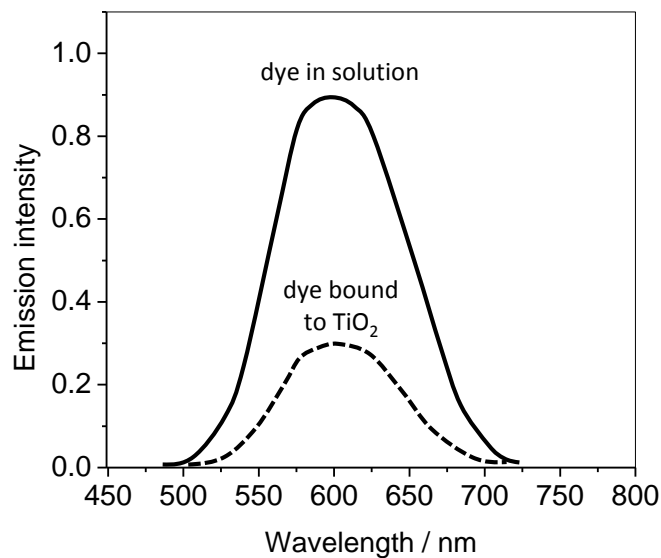
(5 marks)

QUESTION CONTINUED OVERLEAF

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

- i) The emission from a ruthenium dye is quenched via electron transfer when the dye is covalently attached to TiO_2 as illustrated in Figure 1.

Figure 1



From this data estimate the yield of electron transfer assuming unimolecular photochemistry. If $k_o = 4.5 \times 10^8 \text{ s}^{-1}$ for the dye what is the rate constant for electron transfer?

(5 marks)

- ii) Give the equation for Fermi's Golden rule, defining all the terms. With reference to Fermi's Golden rule, briefly describe the factors that influence the rate constant for intersystem crossing.

(5 marks)

2.P1 – Thermodynamics

Answer part a) **AND** either part b) **OR** part c) of this question.

Clearly define all terms and symbols that you use

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

i) The internal energy U of an ideal gas does not change under an isothermal expansion. Explain why. (3 marks)

ii) What is the meaning of ‘chemical potential’? (4 marks)

iii) Derive an expression for the enthalpy change upon heating a substance from one temperature to another.

Assume that there are no phase changes and that its heat capacity is temperature independent (3 marks)

iv) Using the expression you derived from question iii) above calculate the total enthalpy change when 2 moles of water at 80°C is heated to 120°C at constant pressure. (5 marks)

The heat capacity of water is $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$
Heat of vaporization is $40.66 \text{ kJ mol}^{-1}$
Heat capacity of steam is $37.5 \text{ J K}^{-1} \text{ mol}^{-1}$

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

The Gibbs Phase Rule states that:

$$F = C - P + 2$$

i) Define each term in the Phase Rule. (2 marks)

ii) Give the number of phases that can coexist for a binary mixture and explain your reasoning. (2 marks)

iii) Partially miscible liquids tend to become miscible at higher temperatures. Explain this observation. (2 marks)

QUESTION CONTINUED OVERLEAF

- iv) Sketch a typical vapour pressure diagram for a binary mixture indicating the various regions and any salient elements of the figure. (4 marks)

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

- i) Drowning occurs when the lungs fill with water which prevents breathing. Use the Young-Laplace equation to calculate the excess pressure within the water droplets inside the lungs once a victim in danger of drowning is retrieved from the water. (3 marks)

(Alveoli have a mean diameter of 200 microns; The surface tension of water is approximately 70mN.m^{-1} and the Young-Laplace Equation is $\Delta P = 2\gamma/r$)

- ii) The effect of applied pressure on the vapour pressure p of a liquid is given by:

$$p = p^* e^{V_m \Delta P / RT}$$

Combine this expression with the Young-Laplace equation to obtain the Kelvin equation for the vapour pressure above a liquid droplet.

(2 marks)

- iii) Using the result of ii), calculate the increase in water vapour pressure above the droplets within the alveoli (take R as 8 J/K and T as 300K) (3 marks)

- iv) After water has been removed from the lungs a victim can still have trouble with breathing. Give a possible explanation for this phenomenon. (2 marks)

2.P2 – Electrochemistry and Electrochemical Kinetics

Answer **ALL** parts of this question.

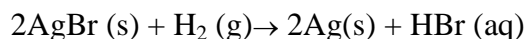
a) Answer **ALL** parts of this question.

For the following situations which (if any) of the specified quantities is largest? Explain clearly the reasoning for your choice.

- i) The cathodic overpotential to obtain a specific current for a reaction occurring at an electrode where the symmetry factor (α) is 0.75 or 0.25? Assume that no other parameters associated with the electrode process change.
- ii) The activity of the acetate ion in a solution of 0.01M acetic acid or the concentration?

(8 marks)

b) Devise a cell (i.e. write out two half cells) for which the electrode reaction is as shown below.

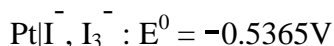
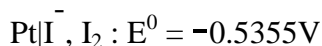


(4 marks)

c) Answer **EITHER** part i) **OR BOTH** parts ii) **and** iii) of this question.

Note: In this question there are very similar potential values and very similar chemical symbols – take care!

For iodine in its different oxidation states, two half-cell potentials are noted below.



The solubility of iodine in water is $1.33 \times 10^{-3} \text{ mol dm}^{-3}$. Assume a temperature of 25°C .

- i) What is the concentration of the triiodide ion (I_3^-) in a saturated solution of iodine in water at 25°C when the concentration of the iodide ion (I^-) is 0.5 mol dm^{-3} ?

(13 marks)

QUESTION CONTINUED OVERLEAF

There is great interest in developing fuel cells and recent work has examined whether some electrode materials might offer better performance if employed in alkaline solutions rather than acid solutions.

- ii) For the reduction of protons to hydrogen, what is the equilibrium potential for the process at pH 13, assuming that the pressure of hydrogen gas is 1 atmosphere?

$$E^0 (\text{H}^+/\text{H}_2) = 0.0\text{V}$$

(4 marks)

- iii) A one electron reduction is carried out at 25°C and has a symmetry factor α equal to 0.5 (irrespective of the electrode material). How much extra overpotential is required for the electrode to pass 50 mAcm⁻² at Au rather than Pt? Assume that the necessary overpotential is greater than -0.1V.

(9 marks)

Electrode Material	$-\log_{10}(j_0 / \text{Acm}^{-2})$
Platinum	3.1
Gold	5.4

2.P5 – Spectroscopy and Characterisation

Answer any **TWO** of parts a), b) **OR** c) of this question.

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

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ gives rise to a UV-vis spectrum in aqueous solution.

i) **Identify** the ground state and the spin allowed transitions using term symbols. (4 marks)

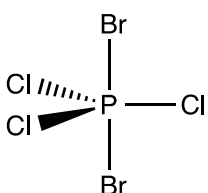
ii) **Show** using direct products how each excitation is linked to a specific electronic configuration in the $(t_{2g})^x(e_g)^y$ format.

$$(t_{2g})^2 = {}^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g} \text{ and } (t_{2g})^3 = {}^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g} \quad (4 \text{ marks})$$

iii) **Sketch**, labelling key features, the uv-vis spectrum of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$. **Discuss** the relative intensity of the expected transitions. (4.5 marks)

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

The reducible representation Γ_{3N} for D_{3h} trans- PCl_3Br_2 is provided below.

D_{3h}	E	C_3	C_2	S_h	S_3	S_6	
Γ_{3N}	18	0	-2	4	-2	4	

i) $\Gamma_{3N} = 2A_1' + A_2' + 4E' + \mathbf{X}A_2'' + 2E''$ Complete the reduction of Γ_{3N} by determining **X**, show your working. (3 marks)

ii) **Determine** Γ_{vib} for trans- PCl_3Br_2 (2 marks)

iii) The cis- PCl_3Br_2 isomer has C_{2v} point group symmetry and Γ_{vib} is given below

$$\Gamma_{\text{vib}} = 5A_1(\text{IR, pol}) + A_2(\text{depol}) + 3B_1(\text{IR, pol}) + 3B_2(\text{IR, pol})$$

Describe key features of the IR and Raman spectra of cis- and trans- PCl_3Br_2
How could the experimental spectra be used to distinguish these isomers? (7.5 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts. Consider the following expression

$$G^A \hat{=} \left\{ G^{\langle f|} \ddot{A} G^m \ddot{A} G^{|i\rangle} \right\}$$

i) Starting from this expression **explain** how we arrive at the rule “a mode is infrared active if the irreducible representation (IR) of the vibration is the same as one of the IRs of the infrared active if the irreducible representation (IR) of the vibration is the same as one of the IRs of the translational vectors”.
(6 marks)

ii) Employ this expression to **determine** if the B_{1g} vibrational mode is IR or Raman active for the D_{4h} point group. **Show your working**
(6.5 marks)