IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 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 IIIA

Physical Chemistry

Thursday 12th January 2012, 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.

3P4 – Statistical Thermodynamics

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

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

i) Calculate the rotational partition function for one molecule of HCl at 100 K and also for one molecule of H_2 at 100 K.

For which of the two molecules is the classical limit approximation less accurate in predicting the rotational contribution to the thermodynamic properties? Justify your answer.

[Data: $m_H = 1$ gmol^{-1}, $m_{Cl} = 35.5$ gmol^{-1}, bond length H_2= 0.74 Å, bond length HCl =1.27 Å, $q_r = \frac{8\pi^2 I k_B T}{\sigma h^2}$]

(5 marks)

ii) Write the statistical thermodynamics equation for the equilibrium constant of the ionization process, Li $\rightarrow$ $Li^+ + e^-$. Define all the terms in your equation.

(2 marks)

iii) For the ionization process, Li $\rightarrow$ $Li^+ + e^-$, calculate the electronic partition functions of the reactants and products.

(3 marks)

iv) The Einstein model for a harmonic solid in three dimensions provides a quantitative description of the heat capacity of solids over a wide range of temperatures.

Sketch the temperature dependence of the heat capacity for this model, indicating the temperature that signals the onset of classical behaviour.

What is the limiting behavior of the model at T$\rightarrow$0 and T$\rightarrow\infty$? How does the high temperature limit compare with the result predicted by the equipartition principle?

(5 marks)

[Data: $C_V = 3R\left(\frac{q_V}{T}\right)^2 \frac{\exp(q_V/T)}{(\exp(q_v/T)-1)^2}$]

QUESTION CONTINUED OVERLEAF

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

Assume that a molecule can access two energy levels, with energies 0 and E for the ground and the excited energy levels respectively.

i) Write the partition function for N "distinguishable" molecules.

(3 marks)

ii) Derive the canonical ensemble equation describing the average energy of the two energy level system given above.

Include in your answer a sketch of the variation of the energy with temperature. Your answer should also include the limiting behaviour of the energy at very low and high temperatures.

(5 marks)

iii) Using the Boltzmann equation, calculate the entropy of 1 mol of sample in the high temperature limit.

(2 marks)

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

Consider one Argon atom confined in a nanopore of length 10 nm. Assume the pore is very narrow and the atom can move in one dimension only.

[Data: m_{Ar} = 39 g/mol, $q^t = \left(\frac{2\pi m k_B T}{h^2}\right)^{D/2} L^D$]

i) Estimate the temperature at which quantum effects are expected to become significant.

You can assume that quantum effects become significant when the number of accessible energy levels is < 100.

(3 marks)

ii) Assuming ideal behavior derive the equation that describes the internal energy inside the nanopore for 1 mol of atoms.

Discuss your result in terms of the equipartition principle.

(7 marks)

3.P3 – Molecular Reaction Dynamics

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

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

Consider a gas phase unimolecular reaction that follows the Lindemann-Hinshelwood mechanism:

i) Derive the rate law for this reaction explaining all stages of the derivation of the rate expressions used.

(4 marks)

ii) Determine the rate constant for the activation step in this reaction, if the effective rate constant is 1.7 x 10^{-3} s^{-1} at 1.09 kPa and 2.2 x 10^{-4} s^{-1} at 25 Pa.

(4.5 marks)

iii) Explain the observation that the order of the reaction rate changes from first order to second order as the pressure changes from a high pressure to a low pressure regimen. Show the derivations of the rate expressions used.

(4 marks)

b) 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 the electron donors and electron acceptors. Show how you would use this data to determine the value of the electron tunnelling coefficient of the protein environment. Explain all stages of the workings and define each symbol used.

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

(9.5 marks)

ii) Explain the Hammond postulate.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

i) Consider a diatomic molecule involved in a collinear collision with an ion. It is found that increasing the translational energy of the reactants has little effect on the yield of products. Using drawings of potential energy surfaces, explain this observation in terms of classical mechanics and discuss the effect of increasing the vibrational energy of the reactants.

(7 marks)

ii) Derive the relationship between equilibrium constant and the degeneracies of the reactant and product states, with reference to the entropy difference between the reactant and product states. Define all symbols.

(5.5 marks)

3.P9 – Photochemistry

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

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

i) Define the following terms:

- Singlet and triplet states.
- Internal conversion.
- Intersystem crossing.
- Fluorescence.
- Phosphorescence.

Briefly discuss the factors that influence the rate of intersystem crossing.

(6 marks)

ii) A porphyrin has a natural radiative lifetime of 24 ns. In solution, this porphyrin is observed to exhibit a fluorescence lifetime of 70 ps. What is the fluorescence quantum yield?

(2 marks)

iii) $S_1 \rightarrow S_0$ fluorescence bands are often mirror images of their corresponding $S_0 \rightarrow S_1$ absorption bands. Explain this observation.

(3 marks)

iv) The triplets of compound (A) have a quantum yield of 0.35 for phosphorescence and a measured triplet state lifetime of 2.4×10^{-3} s. If its phosphorescence is quenched by compound (Q) with a diffusion-controlled rate constant of 10^{10} M^{-1} s^{-1}, what concentration of quencher is required to quench the phosphorescence by half?

(5 marks)

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

i) How many photons are there in a light pulse of energy 350 μJ at a wavelength of 540 nm?

(2 marks)

ii) Describe the mechanisms of Type I and Type II photodynamic action, and summarise the factors which result in a molecule being an efficient sensitizer. Briefly describe how photodynamic action can be used in the treatment of cancer.

(7 marks)

QUESTION CONTINUED OVERLEAF

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

i) Discuss the role of carotenoids in photosynthesis.

(6 marks)

ii) An energy donor (X) has a fluorescence quantum yield of 0.8 in aqueous solution. Compound (Y) is a quencher of fluorescence. When compound (Y) is covalently bound to (X), the fluorescence quantum yield of (X) decreased to 0.26. From these data estimate the efficiency of energy transfer.

(3 marks)