

**DCHA 2705**

**HONOUR SCHOOL OF NATURAL SCIENCE**

**Final Examination**

**GENERAL PHYSICAL CHEMISTRY I**

**Friday, 31st May 2002, 9.30 a.m. to 12.30 p.m.**

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**Answer *FIVE* out of nine questions**

The numbers in square brackets indicate the approximate weight given to each part of the question.

Your attention is drawn to the table of constants provided on page 2 of this paper.

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Do not open this paper until instructed to do so by an invigilator

### Fundamental Constants

Speed of light	$c$	$2.997 \times 10^8 \text{ m s}^{-1}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B$	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F$	$9.649 \times 10^4 \text{ C mol}^{-1}$
Elementary charge	$e$	$1.602 \times 10^{-19} \text{ C}$
Electron mass	$m_e$	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	$m_p$	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	$\epsilon_0$	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Avogadro constant	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	$u$	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	$\mu_B$	$9.274 \times 10^{-24} \text{ J T}^{-1}$

### Other conventions

$P^\ominus$	=	1 bar = $10^5$ Pa	1 atm = 101.325 kPa = 760 Torr
1 Da	=	1 g mol <sup>-1</sup>	1 L = 1 dm <sup>3</sup> 1 M = 1 mol L <sup>-1</sup>

## 1. Atomic Spectroscopy

(a) What are the ground state configurations of, and term symbols for, H and He? [2]

(b) The first excited electronic state of H lies at an energy close to 10.2 eV above the ground state. Electric dipole transitions from the ground state to this excited state are allowed, and at high resolution the associated absorption feature is a doublet.

Identify the electronic configuration of the excited state, and explain the doublet fine-structure observed in the spectrum.

Estimate the ionization energy (in eV) of atomic hydrogen. [5]

(c) The first two excited electronic states of He lie at energies of 19.8 eV and 20.6 eV above the ground state.

Give the configuration and resultant term symbols of the two excited states, and explain why both states revert slowly by radiative decay to the ground electronic state.

Justify the energy ordering of the state assignments you make. [5]

(d) Atomic carbon has low-lying excited electronic states at 0.002 eV and 0.005 eV above the ground state. Two further low-lying excited states are present at 1.2 eV and 2.7 eV. All of these excited states have the same electronic configuration as the ground state.

Explain why the ground electronic configuration leads to several states of different energies. Assign term symbols to these states, and suggest an energy ordering for your assignments.

Allowed transitions are observed from the three lowest states of carbon to excited state(s) with a  $1s^2 2s^2 2p^1 3s^1$  configuration. Identify the excited state(s), and draw a diagram illustrating the transitions involved.

[8]

## 2. Liquid Kinetics

In solution the mechanism for a bimolecular reaction between species A and B may be written



What is meant by the species  $\{AB\}$  appearing in this mechanism? [1]

Derive an expression for the rate constant of a reaction in solution in terms of the elementary processes shown above. Hence explain under what conditions such a reaction would be expected to be diffusion-controlled. [4]

The diffusion-controlled rate constant for a bimolecular reaction between species A and B in solution (expressed in  $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ ) can be written as

$$k_d = 4000\pi r_{AB} D_{AB} N_A f(U)$$

$r_{AB}$  is the encounter distance (expressed in m),  $D_{AB} = D_A + D_B$  is the relative diffusion coefficient (in  $\text{m}^2\text{s}^{-1}$ ) and  $f(U)$  is some function of the interaction potential energy,  $U$ , between the reactants, evaluated at the encounter distance. For reactions between neutral species,  $f(U)$  can be set to unity.

(a) A typical diffusion coefficient for a small molecule in aqueous solution is  $D_A = 2.0 \times 10^{-9} \text{m}^2\text{s}^{-1}$ . Use this value to estimate the diffusion-controlled rate constant for a reaction involving neutral species, assuming an encounter distance of 0.5 nm. [2]

(b) Diffusion-controlled rate constants typically decrease with increasing solvent viscosity and often have activation barriers (typically between  $10 \text{kJ mol}^{-1}$  and  $20 \text{kJ mol}^{-1}$ ). Comment on this observation. [4]

For a reaction between ions in solution

$$f(U) = \frac{U/k_B T}{(e^{U/k_B T} - 1)}$$

where the Coulomb potential can be written as

$$U = \frac{z_A z_B}{\epsilon_r r_{AB}} \frac{e^2}{4\pi\epsilon_0}$$

where  $z_A$  and  $z_B$  are the reactant charge numbers,  $\epsilon_r$  is the relative permittivity, and  $e^2/4\pi\epsilon_0 = 2.307 \times 10^{-28} \text{J m}$ .

(c) Sketch the variation of  $f(U)$  with  $U/k_B T$ , and use it to explain qualitatively the effect charge has on the diffusion rate constant.

Note that  $e^x \simeq (1 + x + \dots)$  for small  $x$ . [5]

(d) Calculate  $f(U)$  for the reaction between solvated electrons and singly charged cations in hexane and in water at 300 K, given the relative permittivities of hexane and water are 1.89 and 78.5 respectively, and assuming an encounter distance of 0.5 nm. Comment on the result you obtain. [4]

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### 3. Statistical Mechanics/Rotational Spectroscopy

Write down an expression for the molecular partition function ( $q$ ) as a sum over *energy levels*, identifying clearly the quantities therein. Explain why  $q$  may be separated into a product of contributions from the various molecular modes of motion. [3]

The rotational energy levels of a (heteronuclear) diatomic molecule are given by  $E_J = Bhc J(J+1)$ , with  $B$  the rotational constant such that  $\theta = Bhc/k_B$  is the characteristic rotational temperature.

(a) Explain why the fraction of molecules found in the rotational energy levels specified by the quantum number  $J$  is

$$f(J) = \frac{(2J+1)}{q_{\text{rot}}} \exp\left(-\frac{\theta}{T} J(J+1)\right)$$

where  $q_{\text{rot}}$  is the rotational partition function. [3]

(b) Write down the expression for  $q_{\text{rot}}$  and, by transforming the sum to a suitable integral, obtain  $q_{\text{rot}}$  in the high-temperature limit  $T \gg \theta$ . [4]

(c) To a first approximation the intensity of a rotational absorption transition from  $J \rightarrow J'$  is determined by  $f(J)$ .

Explain briefly why this is so, and show that the line with maximum spectral intensity ( $J=J_{\text{max}}$ ) corresponds to

$$J_{\text{max}} = \sqrt{\frac{T}{2\theta}} - \frac{1}{2} \quad [5]$$

(d) The Stokes branch of the pure rotational Raman spectrum of the (heteronuclear) molecule consists of approximately equally spaced lines separated by  $9.8 \text{ cm}^{-1}$ . Identify which rotational transition has maximum intensity at a temperature  $T = 298 \text{ K}$ . ( $k_B T/hc = 207.2 \text{ cm}^{-1}$  at  $T = 298 \text{ K}$ ). [5]

#### 4. Polymers/Solution Thermodynamics

- (a) Outline the principles of a simple experiment for measuring the osmotic pressure of a polymer solution. [3]

- (b) Show that the chemical potential,  $\mu_A^*$ , of an incompressible liquid, A, varies with pressure at constant temperature according to

$$\mu_A^*(P) = \mu_A^*(P^0) + V_{A,m}(P - P^0)$$

where  $V_{A,m}$  is the molar volume of A and  $P^0$  is a reference pressure. [2]

By equating the chemical potential in the pure solvent to that in an ideal solution, and taking  $P^0$  to be the pressure above the pure solvent, show that the osmotic pressure  $\Pi = P - P^0$  is given by

$$\Pi V_{A,m} = -RT \ln x_A$$

where  $x_A$  is the mole fraction of A. [2]

Hence show that for a dilute solution ( $x_C = (1 - x_A) \ll 1$ , where  $x_C$  is the mole fraction of the solute, C), the osmotic pressure is given approximately by

$$\Pi = [C]RT$$

where  $[C]$  is the concentration of the solute (in moles per unit volume).

(Note that for  $x \ll 1$ ,  $\ln(1 - x) \approx -x$ .) [3]

- (c) Polymer solutions show deviations from ideality even in dilute solutions, due to the large size of the polymer molecules. The osmotic pressure can then be written as a virial expansion

$$\Pi/[C] = RT(1 + B[C] + \dots)$$

The table below shows the measured osmotic pressure of a solution of PVC in cyclohexanone at 298 K as a function of the concentration,  $c$ , of the polymer in  $\text{kg m}^{-3}$ . By plotting a suitable graph, find the molar mass,  $M$ , of the polymer and the second virial coefficient,  $B$ .

$c/\text{kg m}^{-3}$	1.0	2.0	3.0	4.0	5.0
$\Pi/\text{N m}^{-2}$	11.2	24.9	41.1	60.0	81.2

[8]

- (d) What are the principal physical factors that determine  $B$ ? [2]

## 5. Valence

What is a molecular orbital (MO)? What is the physical justification for approximating a MO as a linear combination of atomic orbitals? [3]

Outline the essential approximations that underlie Hückel theory for the  $\pi$ -electrons of conjugated organic molecules. [4]

Consider now the cyclo-propenium cation  $C_3H_3^+$  within Hückel theory.

(a) Write down the secular equations for  $C_3H_3^+$ , and obtain the corresponding energies in terms of the Coulomb integral ( $\alpha$ ) and resonance integral ( $\beta = -|\beta|$ ). [6]

[You may find it helpful to note that  $x^3 - 3x + 2 = (x - 1)[x(x + 1) - 2]$ .]

(b) Using any suitable method, determine the MO coefficients of the carbon atom  $2p$ -orbitals for the *lowest* energy MO. [4]

For a closed-shell species, the  $\pi$ -electron charge on carbon atom  $i$  is defined by

$$q_i = 2 \sum_{\gamma \text{ occ}} C_{i\gamma}^2$$

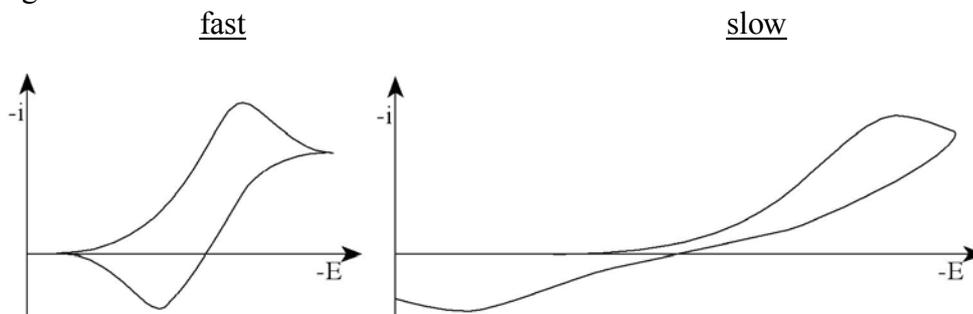
where the MOs are labelled by  $\gamma$ ,  $C_{i\gamma}$  is the MO coefficient on atom  $i$ , and the sum is over all occupied MOs.

(c) Determine  $q_i$  for the carbon atoms in  $C_3H_3^+$ . Suggest how this result might be rationalized in terms of valence-bond structures for the cation. [3]

## 6. Interfacial Kinetics

(a) Explain, without technical details, how a cyclic voltammogram is obtained. [3]

(b) The figures below show typical cyclic voltammograms for 'fast' (reversible) and 'slow' (irreversible) single-electron reductions at an electrode surface.



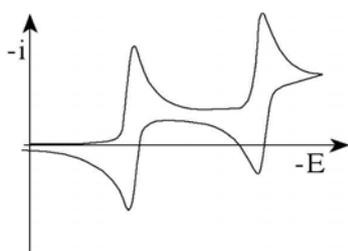
What is meant by 'fast' and 'slow' electron transfer kinetics in the context of cyclic voltammetry? Comment on the different shapes of the two plots. [5]

(c) Typical cyclic voltammograms are shown below for

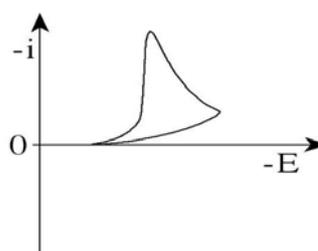
- (i) two sequential, reversible  $1-e^-$  electron transfer reactions
- (ii) an EC reaction with a 'fast' chemical step (where 'E' designates an electron-transfer step and 'C' a chemical step)
- (iii) an ECE reaction
- (iv) a surface-bound electroactive species.

Describe the features of the voltammograms that are characteristic of each process.

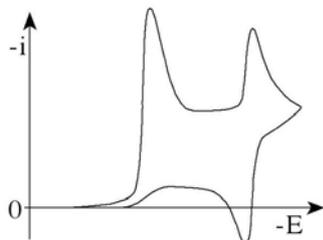
(i)



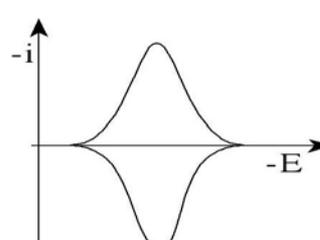
(ii)



(iii)



(iv)



## 7. Reaction rates

The thermodynamic formulation of transition state theory for a gas phase bimolecular reaction may be written

$$k(T) = \frac{k_B T}{h} \times \frac{RT}{P^\ominus} K_P^\ddagger \quad (1)$$

(a) Discuss *briefly* the origin of the factor  $k_B T/h$  appearing in this expression. [3]

(b) (i) The activation energy of a reaction is defined

$$E_a = RT^2 \frac{d \ln k(T)}{dT}$$

Use this equation, together with equation (1), and the van't Hoff equation

$$\frac{d \ln K_P}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

to show that

$$E_a = \Delta^\ddagger H^\ominus + 2RT$$

(ii) Hence show that the Arrhenius  $A$ -factor for a gas phase bimolecular reaction can be written as

$$A = e^2 \frac{k_B T}{h} \frac{RT}{P^\ominus} e^{\Delta^\ddagger S^\ominus / R} \quad (2)$$

where  $RT/P^\ominus$  is typically expressed in units of  $\text{dm}^3 \text{mol}^{-1}$ .

(iii) Briefly explain what is meant by the terms  $\Delta^\ddagger S^\ominus$  and  $\Delta^\ddagger H^\ominus$  appearing in the above equations. [6]

(c) (i) Simple collision theory yields the following expression for the Arrhenius  $A$ -factor, expressed in  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

$$A_{\text{sct}} = 1000 N_A p \sigma \langle c_{\text{rel}} \rangle$$

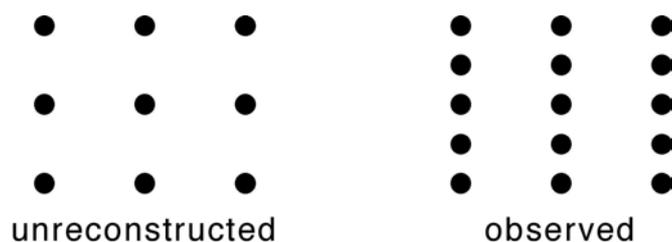
where  $\langle c_{\text{rel}} \rangle = (8k_B T / \pi \mu)^{1/2}$  is the mean relative speed of the reactants (in  $\text{m s}^{-1}$ ),  $\sigma$  is the collision cross-section (in  $\text{m}^2$ ), and  $p$  is the steric factor. Taking  $p = 1$ , and making reasonable estimates for a typical collision cross-section and relative speed at 300 K, estimate  $A_{\text{sct}}$ .

(ii) Use your estimate, together with equation (2), to determine a simple collision theory value for  $\Delta^\ddagger S^\ominus$  at 300 K.

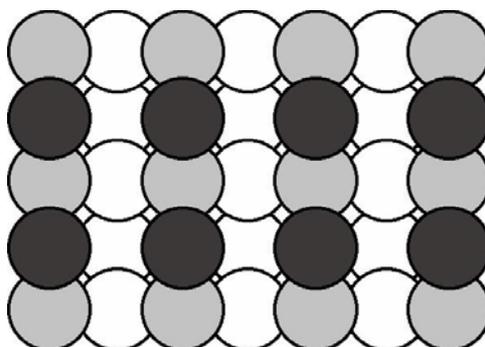
(iii) Account for the sign of  $\Delta^\ddagger S^\ominus$  obtained in (c)(ii). Explain why  $\Delta^\ddagger S^\ominus$  values derived from experimental kinetic data for bimolecular reactions in the gas phase are often more negative than the simple collision estimate, but are rarely less negative. [11]

## 8. Surfaces

- (a) Sketch the atomic arrangements of the (111), (100) and (110) faces of an fcc metal. [5]
- (b) Explain what is meant by the terms *relaxation* and *reconstruction*. [2]
- (c) The LEED pattern expected from the unreconstructed (110) face of Pd is shown below (left) together with the observed LEED pattern (right). Suggest an explanation for this observation. [4]



- (d) Crystalline silicon has the same structure as diamond, in which each atom is covalently bonded to four neighbours in a tetrahedral geometry. The ideal bulk termination of Si(100) is shown below, where the dark grey atoms are in the top layer, the light grey in the second layer and the white atoms in the third and fourth layers.



- (i) How many covalent bonds and how many ‘dangling’ bonds does each surface atom have? [2]
- (ii) LEED and STM show that the surface undergoes a  $(2 \times 1)$  reconstruction. Explain what is meant by the notation  $(2 \times 1)$  and suggest an explanation for the observed reconstruction. [3]
- (iii) Exposure of a reconstructed Si(100)  $(2 \times 1)$  surface to hydrogen atoms leads to adsorption of hydrogen on the surface. Up to a coverage of one hydrogen atom per surface silicon atom the LEED pattern does not change. Further exposure to hydrogen yields a coverage of two hydrogen atoms per surface silicon atom and regenerates a  $(1 \times 1)$  LEED pattern. Suggest explanations for these observations. [4]

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## 9. Properties of Oxygen and its Compounds

Discuss FOUR of the following observations concerning oxygen.

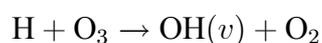
Each part carries equal weight.

(a) In the rotational Raman spectrum of  $O_2$ , only transitions to and from odd  $J$  levels are observed.

(b) Both the quantum yield for formation and the lifetime of triplet states in solution can be sensitive to the presence of dissolved  $O_2$ . Dissolved  $O_2$  can also promote spin-lattice relaxation in NMR.

(c) The vibrational frequency of  $O_2^+$  in its ground electronic state is greater than that in the ground electronic state of  $O_2$ .

(d) The reaction



(which occurs in the stratosphere) leads to a vibrational population inversion in  $OH(v)$ .

(e) The heat capacity of  $O_2$  at constant pressure ( $C_p$ ) takes the following values:

$T/K$	300	2000	3000
$C_p/J K^{-1} mol^{-1}$	29.4	37.8	40.0

[Note that detailed statistical mechanical calculation of the heat capacities is not required, and that  $O_2$  dissociation is not important.]

**[4 × 5]**