

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Monday, 12th June 2000, 2.30 p.m. - 5.30 p.m.

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.

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

1. *Molecular spectroscopy*

- (a) i. State the gross selection rule for observation of a vibration-rotation transition in infrared absorption.
ii. State and justify the selection rules for changes in rotational quantum number in such a transition in linear molecules.

[6]

- (b) Line positions in the fundamental infrared band of a closed shell diatomic are given to a good approximation by the equation:

$$\tilde{\nu}(J', J'') = \tilde{\nu}_0 + B_1 J'(J' + 1) - B_0 J''(J'' + 1)$$

where J' and J'' refer to the rotational quantum numbers in the upper and lower vibrational states respectively.

Lines are found at the following wavenumbers in the fundamental vibration-rotation band of $D^{35}Cl$:

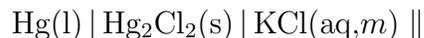
2074.3 2086.0 2107.5 2117.8

- i. Draw a diagram showing the energy levels involved. Identify the lines and determine the constants B_0 , B_1 for $D^{35}Cl$. [7]
ii. Explain why B_1 and B_0 are not the same. Determine the equilibrium bond length r_e from these data. [7]

[Note that in cm^{-1} units $B_e = h/(8\pi^2 cI)$, where c is expressed in cm s^{-1} .]

2. Electrochemistry

- (a) Define the *standard electrode potential*. [2]
- (b) Devise a cell which could be used to measure the standard electrode potential of Ag in equilibrium with an aqueous solution of Ag⁺ ions. Write down the cell reaction and Nernst equation for the cell. [4]
- (c) In modern practice, cell potentials are often measured against a calomel reference electrode, which can be written:



(Calomel is the insoluble mercury (I) chloride.)

- i. Explain why the potential of the electrode depends on the KCl concentration. [3]
- ii. What determines the temperature variation of cell potentials? [3]
- (d) In one form of calomel reference electrode, the KCl is kept in saturated solution by contact with solid KCl. The cell



has a potential of 0.051 V at 298 K. The saturated calomel electrode potential is 0.242 V at this temperature, and the standard electrode potential of the AgCl/Ag couple is 0.222 V.

- i. Obtain the activity coefficient of Cl⁻ ions in 0.08 molal KCl. [4]
- ii. According to the Debye-Hückel limiting law, the activity coefficient in a 0.08 molal KCl solution at 298 K is 0.718. Comment on any difference from the value determined above. [4]

3. Atomic spectra

The ground state of the Ca atom is designated $[\text{Ar}] 4s^2 (^1\text{S})$. The following four excited states are at the approximate wavenumbers given:

$[\text{Ar}] 4s 4p (^3\text{P})$	15200 cm^{-1}
$[\text{Ar}] 4s 4p (^1\text{P})$	23600 cm^{-1}
$[\text{Ar}] 4s 4d (^3\text{D})$	20350 cm^{-1}
$[\text{Ar}] 4s 4d (^1\text{D})$	23000 cm^{-1}

- (a) Explain the meaning of the term symbols. [3]
- (b) Explain why the triplet states are lower in energy than the singlets. [3]
- (c) Both states from the $4s 4p$ configuration are detected in absorption, but the first is seen weakly and the second strongly. The states from the $4s 4d$ configuration are not seen in absorption. Explain these observations. [4]
- (d) The two absorption transitions are both single lines even at high resolution, but the transition between the triplet states, seen in emission, is a multiplet. Explain this difference, and sketch the levels involved in the triplet transitions. [5]
- (e) Two higher states of the Ca atom are as follows:

$[\text{Ar}] 4s 7p (^1\text{P})$	45425 cm^{-1}
$[\text{Ar}] 4s 7d (^1\text{D})$	46310 cm^{-1}

Using the Rydberg constant $\mathcal{R} = 109737 \text{ cm}^{-1}$ and the ionization limit of Ca at 49305 cm^{-1} , determine the effective principal quantum numbers for these two states. Comment on the values you obtain. [5]

4. Photochemistry

(a) Explain the difference between the following:

- i. *Fluorescence* and *phosphorescence*,
- ii. *Radiative lifetime* and *observed emission lifetime*.

[6]

(b) For naphthalene in a glassy matrix at 77 K excited to the S_1 state, the quantum yield of fluorescence is 0.20, the quantum yield of triplet formation is 0.80, and the quantum yield of phosphorescence is 0.018.

- i. Draw a labelled diagram showing the radiative and non-radiative pathways followed in naphthalene under these conditions. [4]
- ii. Using the measured lifetime of fluorescence of 96 ns, determine the rate constant for intersystem crossing from S_1 to T_1 . [3]
- iii. From the measured phosphorescence lifetime of 2.6 s, determine the rate constant for intersystem crossing from T_1 to S_0 . [3]
- iv. Comment on the difference between the two lifetimes and the two intersystem crossing rate constants. [4]

5. *Solution and interfacial kinetics*

- (a) A bimolecular reaction between two species, A and B, in solution can be envisaged as proceeding through an encounter pair {AB} according to the following mechanism:



Explain how this mechanism leads to the concept of *diffusion-controlled* and *activation-controlled* reactions. [4]

What determines the temperature dependence of the rate constant in each case? [2]

- (b) The diffusion-controlled rate constant for reactions between neutral species in solution may be approximated by the Stokes-Einstein-Smoluchowski equation

$$k_d = \frac{8000RT}{3\eta} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

where η is the viscosity of the solvent in Pa s and RT is in J mol^{-1} .

The rate constant for the reaction

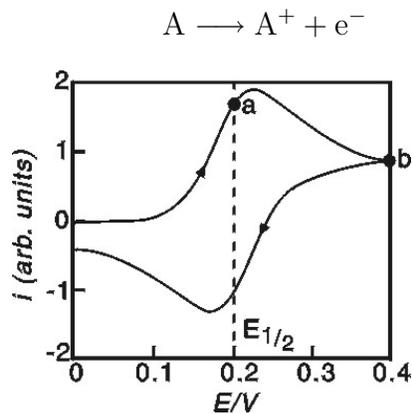


is found to be $1.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Calculate a typical value of k_d from the Stokes-Einstein-Smoluchowski equation and comment on the rate constant for the $\text{H}^+ + \text{OH}^-$ reaction in the light of this value. [4]

[$\eta = 0.89 \times 10^{-3} \text{ Pa s}$ for water at 298 K.]

Suggest a method by which rate constants can be measured for reactions such as $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$. [2]

- (c) The figure below shows the first sweep of a cyclic voltammogram for the oxidation of species A to species A⁺ at an electrode where the kinetics are fast ('reversible' electrode kinetics).



Explain the shape of the voltammogram. Include in your answer a sketch of the concentration profile of A and A⁺ in solution at points **a** and **b** on the voltammogram. You may assume that initially [A] = 1.0 and [A⁺] = 0.0 in arbitrary concentration units. [6]

How would the voltammogram differ if the electrode reaction were slow ('irreversible' electrode kinetics)? [2]

6. Quantum mechanics

- (a) Show, by direct substitution in equation 2, or otherwise, that the Schrödinger equation for a harmonic oscillator of effective mass, m

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \quad (1)$$

can be rewritten as

$$-\frac{1}{2} \frac{d^2\psi}{dq^2} + \frac{1}{2}q^2\psi = E'\psi \quad (2)$$

where the reduced length $q = (km/\hbar^2)^{1/4}x$ and the reduced energy $E' = E/\hbar\omega$, with $\omega = (k/m)^{1/2}$. [4]

- (b) Show that $\psi_0 = Ne^{-q^2/2}$ is a solution to equation (2) and find the corresponding ground state energy, E'_0 , and the normalization constant, N . [6]

$$\left[\text{Note that } \int_{-\infty}^{+\infty} e^{-x^2} dx = \pi^{1/2} \right]$$

- (c) The normalized wavefunctions for the first and second excited vibrational states are

$$\psi_1 = (4/\pi)^{1/4} q e^{-q^2/2} \quad \psi_2 = (1/4\pi)^{1/4} (2q^2 - 1) e^{-q^2/2}. \quad (3)$$

The Hamiltonian for the interaction between a diatomic molecule and an electric field, \mathcal{E} , along the axis of the molecule is

$$H^{(1)} = -\mu\mathcal{E}$$

where μ is the dipole moment of the molecule. The probability per unit time of a transition occurring between $v = 0$ and $v = 1$ is proportional to $|\langle\psi_1|H^{(1)}|\psi_0\rangle|^2$. By expanding the dipole moment as $\mu(q) = \mu_0 + q(d\mu/dq)_{q=0}$ (where μ_0 and $(d\mu/dq)_{q=0}$ are constants), show that

$$|\langle\psi_1|H^{(1)}|\psi_0\rangle|^2 = \frac{1}{2} \left(\frac{d\mu}{dq} \right)_{q=0}^2 \mathcal{E}^2.$$

Comment on this result. [8]

[Note that $\int_{-\infty}^{+\infty} x^2 e^{-x^2} dx = \pi^{1/2}/2$. You may assume that non-degenerate eigenfunctions of a Hermitian operator are orthogonal.]

- (d) By symmetry, or otherwise, show that transitions from $v = 0$ to $v = 2$ are forbidden. [2]

7. Reaction Rates

The transition state theory expression for the rate constant of a gas phase bimolecular reaction between reactants X and Y can be written

$$k(T) = \frac{k_{\text{B}}T}{h} \frac{q^{\ddagger}}{q_{\text{X}}q_{\text{Y}}} e^{-\Delta E_0/RT}$$

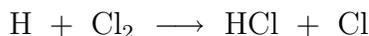
where ΔE_0 is the energy difference between the zero point levels of the reactants and transition state.

- (a) Use this expression to predict the form of the temperature dependence of $k(T)$ for a bimolecular reaction between an atom and a diatomic molecule proceeding *via* a linear transition state. You may set the vibrational partition functions to unity, but should identify any other approximations you employ. [4]
- (b) In terms of partition functions per degree of freedom, what would be the transition state theory expressions for the pre-exponential factor of an atom plus diatomic molecule reaction if it proceeded *via* either (i) a bent transition state (A_{bent}), or (ii) a linear transition state (A_{linear})? Show that the ratio of pre-exponential factors in the two cases may be written

$$\frac{A_{\text{bent}}}{A_{\text{linear}}} \sim \frac{q_{\text{rot}}^{\ddagger}}{q_{\text{vib}}^{\ddagger}}$$

where $q_{\text{rot}}^{\ddagger}$ and $q_{\text{vib}}^{\ddagger}$ are rotational and vibrational transition state partition functions per degree of freedom. [3]

- (c) Consider the kinetic isotope effect for the reaction



- i. Use transition state theory to obtain an expression in terms of molecular partition functions for $k_{\text{H}}/k_{\text{D}}$, the ratio of the rate constant for the hydrogen atom reaction with Cl_2 (k_{H}) to that for the deuterium atom reaction with Cl_2 (k_{D}). [3]
- ii. Explain why q^{\ddagger} is little affected by deuterium substitution at 300 K. You may assume the transition state to be linear. [5]
- iii. At 300 K the experimentally determined kinetic isotope ratio is $k_{\text{H}}/k_{\text{D}} = 1.5$. Discuss the factors which are likely to be responsible for this value. Detailed calculation is not required. [5]

8. Statistical mechanics

- (a) Show that the partition function for a harmonic oscillator is

$$q_{\text{vib}} = (1 - e^{-h\nu/k_{\text{B}}T})^{-1}$$

where ν is the vibrational frequency (in s^{-1}), and the energy of the zero-point level of the oscillator has been defined as zero. [4]

[Note that $1 + x + x^2 + x^3 + \dots = (1 - x)^{-1}$.]

- (b) The Einstein model of a crystal assumes that the atoms are free to undergo independent harmonic vibrational motion along each Cartesian coordinate, x , y , and z .
- i. Show that for a crystal with N atoms, the Einstein model yields the following expression for the internal energy, $U(T)$, at temperature, T ,

$$U(T) - U(0) = 3Nh\nu (e^{h\nu/k_{\text{B}}T} - 1)^{-1}$$

where $U(0)$, is the internal energy of the Einstein crystal at 0 K. [5]

[Remember that $U(T) - U(0) = k_{\text{B}}T^2 (\partial \ln Q / \partial T)_V$, where Q is the canonical partition function.]

- ii. What does $U(T) - U(0)$ equal in the limit of high temperature? Comment on this result. [3]
- iii. What would $U(0)$ have been if the zero of energy, referred to in part (a), had been measured with respect to the bottom of the potential energy well for each oscillator in the crystal? [2]
- iv. Obtain an expression for the molar heat capacity of the model crystal at constant volume, C_V . With the help of a sketch, describe how C_V varies with temperature. Justify, and comment on, the limiting low and high temperature values you show in your sketch. [6]

9. Polymers

- (a) The Random Flight Model is the simplest model for describing the conformations of polymer chains in a solution. A polymer is treated as consisting of N segments each of which is characterized by a vector \mathbf{l}_k of length l . In the Random Flight Model the orientations of these segments are random, i.e. $\langle \mathbf{l}_j \cdot \mathbf{l}_k \rangle = 0$ where j and k are two *different* segments. The vector \mathbf{R} connecting the two ends of the polymer is

$$\mathbf{R} = \sum_{k=1}^N \mathbf{l}_k .$$

Show that the mean square distance between the two ends can be written

$$\langle R^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle = N l^2$$

[3]

Calculate the predicted value, in the Random Flight Model, of the root-mean-square end-to-end distance, $\langle R^2 \rangle^{1/2}$, for polyethylene oxide of molecular weight 10^6 u, taking the segment to be $(\text{CH}_2\text{CH}_2\text{O})$ with a molecular weight of 44 u and a length of 0.36 nm.

[3]

The value of $\langle R^2 \rangle^{1/2}$ inferred from light scattering is 110 nm. Comment on the Random Flight Model in the light of this value.

[4]

- (b) Man-made polymers have several features that distinguish their behaviour from that of small molecules, for example, a high molecular weight, polydispersity, and a large contribution to the standard entropy from different chain conformations. Explain how these factors play a role in *THREE* of the following observations on the behaviour of polymers.
- For most polymers, determination of the molecular weight by osmotic pressure measurements and by light scattering gives different values;
 - Polymer solutions show large deviations from ideality;
 - Rubber warms up if it is stretched adiabatically (for a metal spring, only a very small temperature change is observed);
 - Weakly adsorbed polymers stabilize colloids against coagulation;
 - The radius of gyration of polystyrene in cyclohexane increases with increasing temperature.

[10]