

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Wednesday, 9th June, 2004, 9.20 a.m. to 12.30 p.m.

Candidates should answer *THREE* questions

Please begin your answer to each question in a new booklet.

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

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

1. Valence/Molecular Electronic Spectroscopy
2. Nuclear Magnetic Resonance
3. Ions in Solution
4. Vibration–Rotation Spectroscopy
5. Electronic Spectroscopy and Group Theory
6. Thermodynamics
7. Quantum Mechanics
8. Interfacial Kinetics
9. Statistical Mechanics
10. Atomic Spectroscopy
11. Theories of Kinetics
12. Molecular Reaction Dynamics

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

Fundamental Constants

| | | |
|---------------------|------------------|---|
| Speed of light | c | $2.998 \times 10^8 \text{ m s}^{-1}$ |
| 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 | ϵ_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 | μ_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 |
| m^\ominus | = | 1 mol kg^{-1} | 1 L = 1 dm^3 |
| 1 Da | = | 1 g mol^{-1} | 1 M = 1 mol L^{-1} |

1. Valence/Molecular Electronic Spectroscopy

- (a) What is an orbital? Explain what is meant by the orbital approximation in molecular electronic structure, and why all states arising from a given configuration are degenerate within this approximation. [4]
- (b) Draw a molecular orbital diagram appropriate to the O_2 molecule. Discuss features of note in the diagram and the nature of the molecular orbitals arising. [6]
- (c) Deduce all electronic states that arise from the ground-state configuration of O_2 , explaining carefully the meaning of the term symbols involved. Comment briefly on why these states have different energies. [10]
- (d) Some spectroscopically determined properties of the ground electronic states for the O_2 , O_2^+ and O_2^- molecules are shown below; ω_e denotes the vibrational frequency and B_e the equilibrium rotational constant.

| | $\omega_e(\text{cm}^{-1})$ | $B_e(\text{cm}^{-1})$ |
|--------------|----------------------------|-----------------------|
| $^{16}O_2$ | 1580 | 1.44 |
| $^{16}O_2^+$ | 1905 | 1.69 |
| $^{16}O_2^-$ | 1090 | 1.16 |

The equilibrium bond length of the O_2 molecule is $r_e = 0.121$ nm.

Relate these properties to the character of the molecular orbitals involved in the ground states, and deduce as much information as possible from the data given.

[6]

- (e) The O_2 molecule exhibits an intense electronic transition at $\sim 50,000$ cm^{-1} , due to an allowed $\pi \rightarrow \pi^*$ transition. Determine all possible *triplet* states that arise from the excited electronic configuration. Hence identify the transition observed, giving your reasons. [8]

Turn over.

2. Nuclear Magnetic Resonance

(a) Explain the mechanism of spin–spin coupling in NMR. [4]

(b) A general expression for the energy levels of a group of three weakly coupled spin- $\frac{1}{2}$ nuclei in a molecule is:

$$E(m_1, m_2, m_3) = -m_1\nu_1 - m_2\nu_2 - m_3\nu_3 + J_{12}m_1m_2 + J_{13}m_1m_3 + J_{23}m_2m_3$$

where E is in frequency units and the nuclei are labelled by the subscripts 1, 2 and 3.

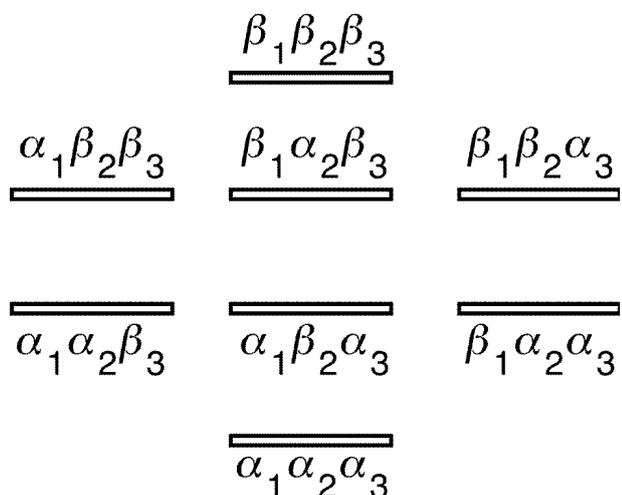
Explain what is meant by the symbols ν_i , J_{ij} and m_i where $i, j = 1, 2$ or 3 . State the allowed values of m_1 , m_2 and m_3 , and explain what is meant by the expression “weakly coupled”. [4]

(c) Derive the following expression for the frequencies of the allowed transitions of nucleus 1:

$$\nu = \nu_1 - J_{12}m_2 - J_{13}m_3$$

and hence show that each nucleus has four allowed NMR transitions. [4]

(d) The energy levels of a group of three spin- $\frac{1}{2}$ nuclei are shown schematically in the diagram



Explain what is meant by the symbols α and β . Make a rough copy of the diagram and indicate on it the allowed NMR transitions, showing clearly which transition belongs to which of the three nuclei. [5]

Question continues.....

(e) Sketch the appearance of the NMR spectrum of nucleus 1 under each of the following conditions:

(i) $J_{12} > J_{13} > 0$,

(ii) $J_{12} = J_{13} > 0$,

(iii) $J_{12} > 0, J_{13} = 0$.

[5]

(f) The ^{19}F spectra of six isomers (A–F) of the substituted benzene $\text{C}_6\text{H}_2\text{FX}_3$ were recorded. X is a substituent containing no magnetic nuclei and ^{19}F is a spin- $\frac{1}{2}$ nucleus. Approximately measured values of J_{12} and J_{13} (in Hz) are given in the table below. Here the label 1 denotes the fluorine, and labels 2 and 3 denote the two protons. Determine possible structures for each of the six isomers, and suggest an experiment that could be done to resolve the ambiguity between B and C.

[7]

| isomer | $ J_{12} $ | $ J_{13} $ |
|--------|------------|------------|
| A | 9 | 9 |
| B | 9 | 6 |
| C | 9 | 6 |
| D | 9 | 0 |
| E | 6 | 6 |
| F | 6 | 0 |

(g) Determine the appearance of the ^{19}F NMR spectrum of the deuterated form of isomer A, $\text{C}_6\text{D}_2\text{FX}_3$. Note that the deuterium nucleus has a spin angular momentum of 1.

[5]

Turn over.

3. Ions in Solution

- (a) The extended Debye-Hückel expression for the logarithm of the mean-ionic activity coefficient, γ_{\pm} , of a 1:1 electrolyte can be written as

$$\log_{10} \gamma_{\pm} = - \frac{A\sqrt{I}}{1 + B\sqrt{I}},$$

where A and B are dimensionless coefficients. Explain what I is, and how it may be calculated in practice. Describe one possible origin of the term $(1 + B\sqrt{I})$, and discuss under what conditions it might become important. [3]

- (b) The osmotic pressure, Π , for a dilute solution of a fully ionized 1:1 electrolyte can be represented by the equation

$$\Pi = \frac{2c\rho RT\gamma_{\pm}}{M}$$

where c is the mass concentration of the solute (g per kg of solvent), M its molar mass, and ρ is the solvent density. Π was measured for a series of such solutions in water at $T = 25^{\circ}\text{C}$, for which ρ can be taken to be 1 kg dm^{-3} , and the results are given in the table.

| | | | | | | |
|-------------------------|-------|------|------|------|-------|-------|
| $c/(\text{g/kg}^{-1})$ | 0.01 | 0.05 | 0.10 | 1.00 | 2.50 | 5.00 |
| $\Pi/(\text{N m}^{-1})$ | 0.834 | 4.09 | 8.08 | 74.2 | 174.8 | 330.1 |

Assuming that the simplified limiting Debye-Hückel expression can be used *for the first three low-concentration points*, estimate the molar mass of the salt, and obtain an estimate of the constant A . [9]

- (c) Calculate Π for an ideal solution (*i.e.* with $\gamma_{\pm} = 1$) at each concentration, and hence, by comparing the measured with the ideal osmotic pressure, determine the activity coefficient for each solution. [4]

Now obtain an approximate value for the parameter B . [3]

In some formulations, B is written as

$$B = a.B'$$

Given that $B' = 0.329 \times 10^{10} \text{ m}^{-1}$, calculate a value for a , and state its units. [3]

Is the value reasonable in the light of your explanation of the term $(1 + B\sqrt{I})$? [3]

Question continues.....

- (d) At substantially higher concentrations than those of the experiments in the table, corresponding to a molality of 5 mol kg^{-1} , the measured mean activity coefficient is 0.80. Discuss this value in relation to the activity coefficients that you have calculated for the lower concentrations. [3]

At this molality, the activity of the *water* (as measured in independent experiments) is roughly 0.81. Explain qualitatively how changes in the activity of the water can be related to changes in the activity of the electrolyte, and show what bearing this discussion has on the activity coefficient for the electrolyte at the concentration of 5 mol kg^{-1} . [3]

A possible explanation for the reduction in activity of water in the presence of the solute is that some 'free' water has been taken up as a sheath of hydration of the solute ions. By calculating the number of moles of water in one litre of pure water, estimate the *hydration number* (the average number of water molecules associated with each solute molecule). [3]

Turn over.

4. Vibration–Rotation Spectroscopy

- (a) State the vibrational and rotational selection rules for (i) vibration–rotation (infrared) spectroscopy and (ii) Raman spectroscopy for a closed-shell, linear molecule. What molecular properties are responsible for infrared and Raman activity? [6]

- (b) CO₂ is a linear molecule with three vibrational frequencies, associated with the symmetric stretching vibration (ν_1), the bending vibration (ν_2) and the antisymmetric stretching vibration (ν_3). The rotational constant in a given vibrational level (v_1, v_2, v_3) is given by

$$B_v = B_e + \alpha_1^B(v_1 + \frac{1}{2}) + \alpha_2^B(v_2 + 1) + \alpha_3^B(v_3 + \frac{1}{2}).$$

For ¹⁶O the nuclear spin I is zero.

The first few lines in the rotational Raman spectrum of CO₂, excited with a laser of frequency ν_{ex} cm⁻¹, are measured to be (in cm⁻¹)

$$\nu_{\text{ex}} - 5.4629, \nu_{\text{ex}} - 2.3413, \nu_{\text{ex}}, \nu_{\text{ex}} + 2.3413, \nu_{\text{ex}} + 5.4629.$$

Draw an energy-level diagram to show how these transitions arise. Hence determine the rotational constant for CO₂ in its ground state, B_0 ; centrifugal distortion effects can be ignored. [8]

- (c) Lines near the centre of the vibrational Raman band of CO₂, excited with the same laser, are measured to be (in cm⁻¹)

$$\nu_{\text{ex}} - 1393.6087, \nu_{\text{ex}} - 1390.5040, \nu_{\text{ex}} - 1388.1700, \nu_{\text{ex}} - 1385.8287, \nu_{\text{ex}} - 1382.6998.$$

Explain why the rotational spacings in this spectrum differ from those in (b). Use the method of combination differences to determine values for ν_1 and B_v (for $v_1 = 1$) and hence for α_1^B . [6]

- (d) The first few lines near the centre of the lowest frequency band in the vibration–rotation spectrum of CO₂ occur at the following wavenumbers (in cm⁻¹):

$$664.2890, 665.8426, 667.4020, 668.1839, 669.7519.$$

Assign these lines and use the measurements to determine the values for ν_2 and α_2^B . [6]

- (e) Explain why α_1^B is negative while α_2^B is positive. [3]

- (f) In the vibration–rotation spectrum, in addition to the ν_2 and ν_3 fundamental bands, a weak band is observed at 2051.092 cm⁻¹. Explain how this band arises. Why does it occur at a different wavenumber from that expected from parts (c) and (d) above? Would you expect to see a Q-branch in this band? Give your reasons. [5]

5. Electronic Spectroscopy and Group Theory

- (a) The molecule formaldehyde H_2CO is planar in its ground $^1\text{A}_1$ electronic state and so displays the symmetry of the point group C_{2v} . In what follows, take the out-of-plane axis to be the x -axis and the two-fold axis of symmetry to be the z -axis. By considering the three cartesian displacements of each atom, show that the six vibrational modes of the molecule form the bases for three A_1 , one B_1 and two B_2 irreducible representations. You may find it helpful to take sum and difference combinations of the displacements of the two H atoms to reflect the symmetry of the group. [12]
- (b) Explain what is meant by the statement that an electronically forbidden transition in a polyatomic molecule can still be observed if it is vibronically allowed. [4]
- (c) The first electronic transition of H_2CO in the near-ultraviolet from the ground $^1\text{A}_1$ state is formally to a $^1\text{A}_2$ state. Show that such a transition is electronically forbidden. Analysis of the rotational structure in this transition shows that the transition moment lies along the y -axis. By which vibration(s) is vibronic intensity conferred? [6]
- (d) The first vibrational band in the vibronically induced absorption spectrum of H_2CO in the near-ultraviolet lies at $28\,871\text{ cm}^{-1}$. The first two bands in the emission spectrum, starting from the $v' = 0$ level, lie at $27\,021\text{ cm}^{-1}$ and $24\,687\text{ cm}^{-1}$. Explain these observations with the help an energy-level diagram. Determine the band origin of the electronic transition and the wavenumber of the vibrational mode in the excited electronic state that is responsible for the vibronically induced intensity. [12]

The vibrational wavenumbers of H_2CO in its ground electronic state are:

$$\begin{aligned}\nu_1 &= 2766\text{ cm}^{-1}(\text{A}_1) \\ \nu_2 &= 1746\text{ cm}^{-1}(\text{A}_1) \\ \nu_3 &= 1501\text{ cm}^{-1}(\text{A}_1) \\ \nu_4 &= 1167\text{ cm}^{-1}(\text{B}_1) \\ \nu_5 &= 2843\text{ cm}^{-1}(\text{B}_2) \\ \nu_6 &= 1251\text{ cm}^{-1}(\text{B}_2)\end{aligned}$$

Turn over.

6. Thermodynamics

- (a) For a simple one-component substance, sketch a typical phase diagram in the (P, T) -plane, indicating clearly the critical and triple points occurring at $T = T_c$ and T_t respectively. Illustrate also the qualitative behaviour of isotherms in the (P, V) -plane, for a representative range of temperatures $T > T_t$. Discuss features of note in your diagram. [6]

- (b) The van der Waals equation of state is given by

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

(where V denotes the molar volume). a and b are the van der Waals constants and $b = (4\pi r^3/3)N_A$ may be employed to define an effective molecular radius, r . The critical point, at (P_c, V_c, T_c) , is defined by $(\partial P/\partial V)_T = 0 = (\partial^2 P/\partial V^2)_T$.

Show that

$$V_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

Hence show that the equation of state in reduced variables, $p = P/P_c$, $v = V/V_c$ and $t = T/T_c$, is given by

$$p = \frac{8t}{3v - 1} - \frac{3}{v^2}$$

Comment on the fact that the van der Waals constants no longer appear in this expression. [9]

- (c) For Ne and Xe, the experimental P_c and T_c are given by Ne: $P_c = 26.9$ atm, $T_c = 44.4$ K; Xe: $P_c = 58.0$ atm, $T_c = 289.8$ K. Assuming the van der Waals equation of state, determine the relative ratio of each van der Waals constant for Ne and Xe. Discuss your result qualitatively in relation to the intermolecular interactions between noble-gas atoms, and to the fact that the ratio of the van der Waals radii for Xe and Ne in the solid state is $\simeq 1.4$. [8]

- (d) The isothermal compressibility \mathcal{K}_T is given by $\mathcal{K}_T = -\frac{1}{V}(\partial V/\partial P)_T$. For the van der Waals equation of state, show that

$$P_c \mathcal{K}_T = \frac{1}{6} \left[\frac{4tv}{(3v - 1)^2} - \frac{1}{v^2} \right]^{-1}$$

[6]

- (e) At the critical volume, where $v = 1$, sketch the temperature dependence of \mathcal{K}_T for $t = T/T_c > 1$. Comment on the behaviour arising, and relate it to your answer to part (a) above. [5]

7. Quantum Mechanics

- (a) Treating the nucleus as infinitely heavy, write down the Hamiltonian $\hat{H}_0 \equiv \hat{H}_0(\mathbf{r}; Z)$ for a one-electron atomic ion with arbitrary nuclear charge Z . [2]

- (b) The ground state wavefunction for \hat{H}_0 is

$$\Phi(r) = N \exp(-Zr/a_0)$$

with a_0 the Bohr radius. The corresponding energy is $-Z^2/2$ in units of the Hartree ($E_h = e^2/(4\pi\epsilon_0 a_0) = 27.21\text{eV}$).

Show that the normalization constant $N = (Z^3/\pi a_0^3)^{1/2}$, and that the expectation value $\langle 1/r \rangle = Z/a_0$. Note that [4]

$$\int_0^{\infty} r^n e^{-br} dr = \frac{n!}{b^{n+1}}.$$

- (c) Write down the Hamiltonian for the Li^+ ion. Re-express your answer in the form $\hat{H} = \hat{H}_0(\mathbf{r}_1; Z) + \hat{H}_0(\mathbf{r}_2; Z) + \hat{V}$ where, as in part (a), $\hat{H}_0(\mathbf{r}_i; Z)$ refers to a one-electron ion with *arbitrary* charge Z . State explicitly your expression for \hat{V} . [5]

- (d) Explain briefly what is meant by the Variational Principle and why it is important in quantum mechanics. [5]

- (e) A simple variational wavefunction for the Li^+ ion is given in standard notation by

$$\Psi = \Phi(r_1)\Phi(r_2) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

where $\Phi(r)$ is as in part (b) and Z represents the effective, screened nuclear charge, which remains to be determined.

Explain in physical terms why you expect Z to lie in the range $2 < Z < 3$. [4]

- (f) With r_{12} denoting the magnitude of the inter-electron separation in Li^+ , the expectation value $\langle 1/r_{12} \rangle = 5Z/8a_0$. Use results from part (b) to show that the expectation value of the Hamiltonian is given by $E(Z) = Z^2 - 43Z/8$ in Hartrees. Hence determine the effective nuclear charge for the Li^+ ion, and comment on your answer. [8]

- (g) By considering the ionization potential of Li^{2+} , use your answer to part (f) to estimate the second ionization potential of the Li atom, the experimental value for which is 75.64 eV. Compare and contrast your answer to the estimate obtained if screening in Li^+ is neglected. [6]

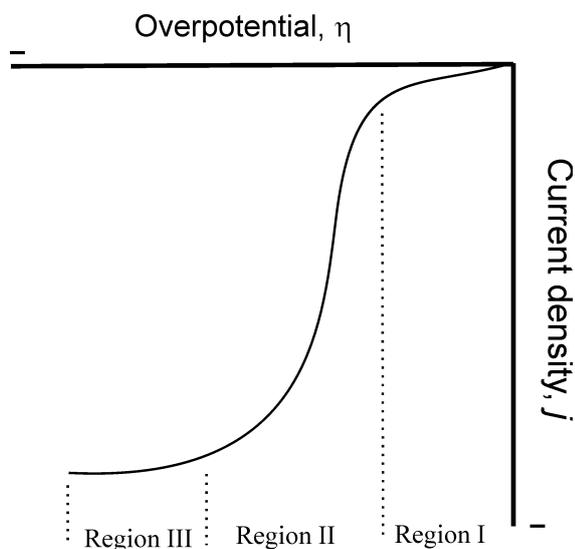
Turn over.

8. Interfacial Kinetics

- (a) What is meant by the terms *overpotential* (η) and *exchange current density* (j_0)? [4]

What does the exchange current represent in physical terms? [3]

The figure shows the current density measured at an electrode of an electrochemical cell as a function of (negative) overpotential. Explain qualitatively the appearance of the curve, and account for the existence of the three regions indicated on the figure. [4]



- (b) For some values of the overpotential, the cathodic current density, j_c , can be described in terms of an activated kinetic process in which the rate constant is given by the equation

$$k_c = B_c \exp\{-(\Delta^\ddagger G_c(0) + \alpha F \Delta\phi)/RT\}.$$

Explain what the terms α and $\Delta\phi$ are, and use the equation to show that j_c is given by the expression

$$j_c = j_0 \exp(-\alpha F \eta / RT). \quad [6]$$

For which region of the curve in the figure does this expression approximately describe the total current density? [2]

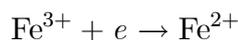
Question continues.....

- (c) Measurements were made of the cathodic current, i_c , at a Pt electrode of area 3 cm^2 immersed in a solution containing Fe^{2+} and Fe^{3+} ions at different values of the overvoltage, η . The data are shown in the table for experiments conducted at $T = 298\text{K}$.

| | | | | |
|-----------------|-------|-------|--------|--------|
| η/V | -0.05 | -0.10 | -0.15 | -0.20 |
| i_c/mA | -19.9 | -70.4 | -221.6 | -687.2 |

From these data, calculate j_0 and α . Comment on your value of α , and explain what determines its magnitude. [8]

- (d) The reaction



occurs at the cathode of the cell just described. According to Fick's first law of diffusion, the flux of ions, J , is proportional to the concentration gradient, $\partial c/\partial x$

$$J = -D(\partial c/\partial x)$$

if the transport of ions to the electrode is diffusion limited. Assuming that c decreases linearly from the bulk value to zero over a diffusion layer of thickness 0.01 mm , and that the diffusion-limited current density is $-685.2 \text{ mA cm}^{-2}$ for an electrolyte concentration of 1 mol dm^{-3} , calculate the diffusion coefficient, D , for Fe^{3+} in water. [7]

Turn over.

9. Statistical Mechanics

- (a) State how the Helmholtz free energy is related to the canonical partition function Q . Using this result, show that the chemical potential for species α is given by $\mu_\alpha = -RT(\partial \ln Q / \partial N_\alpha)$ where N_α is the number of molecules of species α . [4]
- (b) Two isomers, A and B , are in equilibrium in the gas phase. The canonical partition function is

$$Q = \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

and the molecular partition function q_α (for species $\alpha = A$ or B) is given by $q_\alpha = q_{\text{tr}} q_{\text{int}} \exp(-E_\alpha/k_B T)$. Here $q_{\text{tr}} = V/\Lambda^3(T)$ where $\Lambda(T)$ is the de Broglie wavelength for an isomer and $V = [(N_A + N_B)k_B T]/P$ is the volume. $q_{\text{int}}(T)$ denotes contributions arising from internal degrees of freedom, taken to be the same for both species; E_α is a constant, with $E_A \neq E_B$.

Show that the chemical potential for species α in the gas phase is given by

$$\mu_\alpha = -RT \ln(q_\alpha/N_\alpha). \quad [5]$$

[Stirling's approximation for large M is $\ln(M!) = M \ln(M) - M$.]

- (c) The gases are also in equilibrium with a solid surface containing N lattice sites. The canonical partition function for the solid is

$$Q = \frac{N!}{N_A! N_B! [N - (N_A + N_B)]!} q_{A,s}^{N_A} q_{B,s}^{N_B}$$

N_A, N_B here denote the number of isomers adsorbed on the surface, with surface coverage $\theta_\alpha = N_\alpha/N$ ($\alpha = A$ or B). The molecular partition functions for the solid are given by $q_{\alpha,s} = q_{\text{int}}(T) \exp(-e_\alpha/k_B T)$, with $q_{\text{int}}(T)$ as specified above; e_α is a constant, with $e_A \neq e_B$.

Show that the chemical potential $\mu_{\alpha,s}$ of species α in the solid phase is given by

$$\mu_{\alpha,s} = RT \ln \left[\frac{\theta_\alpha}{1 - (\theta_A + \theta_B)} \frac{1}{q_{\alpha,s}} \right].$$

By equating the chemical potentials in the solid and gas phases, show that the surface coverage is given by

$$\frac{\theta_\alpha}{1 - (\theta_A + \theta_B)} = K_\alpha(T) P_\alpha$$

and obtain an explicit expression for $K_\alpha(T)$. Here, $P_\alpha = x_\alpha P$ is the partial pressure of gas-phase species α . Comment briefly on the result for θ_α . [10]

Question continues.....

(d) Show that if $E_A - E_B = e_A - e_B$, the total surface coverage $\theta = \theta_A + \theta_B$ is given by the one-component Langmuir form $\theta = KP/(1 + KP)$; give your expression for $K(T)$. [5]

(e) State how the internal energy is related to the canonical partition function, and how the entropy is related to the internal energy and Helmholtz free energy. Given that $q_{\text{int}}(T) = \exp(-\varepsilon/k_B T)$ at low temperatures, show that the entropy at $T = 0$ in the solid phase is given by

$$S(0) = -Nk_B [\theta_A \ln(\theta_A) + \theta_B \ln(\theta_B) + (1 - [\theta_A + \theta_B]) \ln(1 - [\theta_A + \theta_B])].$$

Discuss the physical interpretation of this result. [10]

Turn over.

10. Atomic Spectroscopy

- (a) \hat{P}_{12} is an operator that permutes identical particles in a quantum system

$$\hat{P}_{12}\Psi(1, 2) = \Psi(2, 1)$$

where 1 and 2 describe both spatial and spin coordinates of the two particles. State the Pauli Exclusion Principle in terms of this operator. [2]

- (b) Determine which *triplet* electronic states can arise for the ground configuration $3d^24s^2$ of the titanium atom by restricting your attention to those states with $M_S = +1$ only. Note that terms with $L = 3$ and 4 are referred to as F and G states, respectively. [10]

Explain why the ground electronic state (term) of Ti is 3F . What are the J -values of the different spin components (levels) of the 3F state, and what is their energy ordering? [4]

- (c) Spin-orbit coupling in an atom is represented by the operator $\hat{H}_{so} = A\hat{L}\cdot\hat{S}$. Show that this operator makes a contribution

$$E_{so} = \frac{1}{2}A[J(J+1) - L(L+1) - S(S+1)]$$

to the energy of a level L, S, J that follows Russell-Saunders coupling. The separation between the two lowest J -levels of Ti in its ground state is 170.32 cm^{-1} . Predict the other spin-orbit splittings for this ground state. [5]

- (d) A sample of Ti atoms is placed in a variable magnetic field B_Z and irradiated with a fixed-frequency laser producing far-infrared radiation with a wavenumber equal to 170.653 cm^{-1} . Transitions between the individual M -levels of the two lowest spin components of the ground state are tuned into resonance with the laser frequency ν_L according to

$$\nu_L = \nu_0 + (g'_J M'_J - g''_J M''_J)\mu_B B_Z$$

In this equation, ν_0 is the zero-field transition wavenumber, μ_B is the Bohr magneton, g_J is the Landé g -factor and M_J is the laboratory-fixed component quantum number. The ' and '' labels refer to the upper and lower levels of the transition. The magnetic field is oriented so that only $\Delta M_J = \pm 1$ transitions can be induced. Draw a diagram to show how the energies of the M -states of the two levels involved vary with magnetic field. On this diagram, draw in the allowed transitions with either $\Delta M_J = +1$ or -1 . [5]

Question continues.....

One of the transitions, which can be detected in such an experiment, is between $M'_J = 3$ and $M''_J = 2$. Predict the magnetic field strength required to make this transition resonant with the laser. [8]

It may be useful to recall that

$$\mu_B \equiv 0.46686 \text{ cm}^{-1}\text{T}^{-1} \text{ and } g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

Turn over.

11. Theories of Kinetics

- (a) State the Arrhenius equation that relates the rate constant, k_2 , for an elementary bimolecular reaction to the temperature, and show that

$$E_a = RT^2 \{d \ln k_2 / dT\}$$

where E_a is the experimental activation energy. [1]

The simple hard-sphere collision theory of reaction kinetics predicts that k_2 for reaction between partners X and Y should be given in units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ by

$$\begin{aligned} k_2 &= Z'_{XY} \exp(-E_c/RT) \\ &= \pi(r_X + r_Y)^2 \bar{c} \exp(-E_c/RT) \times (1000N_A) \end{aligned}$$

with $\bar{c} = (8k_B T/\pi\mu)^{1/2}$, where r_X , r_Y are the hard-sphere collision radii of X and Y, and μ is their reduced mass.

What is the meaning of the quantity E_c ? Show the correspondence of this equation to the Arrhenius equation, and relate E_a to E_c . [4]

Calculate Z'_{XY} for the reaction



at $T = 298 \text{K}$ in units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. The collision radii of OH and CHCl_3 are 0.16 nm and 0.26 nm; take the relative atomic mass of Cl to be 35.5. [4]

The pre-exponential factor, A , of the Arrhenius equation determined experimentally is $1.3 \times 10^9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Calculate the ratio A/Z'_{XY} , and comment on the value. [2]

- (b) Transition-state theory, expressed in terms of classical thermodynamic quantities, predicts that

$$k_2 = (k_B T/h)(1/c^\ominus) \exp(-\Delta^\ddagger G^\ominus/RT)$$

where $\Delta^\ddagger G^\ominus$ is the standard free energy of activation, and c^\ominus is the standard state concentration to which $\Delta^\ddagger G^\ominus$ is referred (1mol dm^{-3} if k_2 is to be in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$).

Using the definition of free energy, rewrite the equation in terms of $\Delta^\ddagger H^\ominus$ and $\Delta^\ddagger S^\ominus$, and also in terms of $\Delta^\ddagger U^\ominus$ and $\Delta^\ddagger S^\ominus$. [5]

Assume that $\Delta^\ddagger U^\ominus$ and E_c are identical, and estimate the entropy of activation $\Delta^\ddagger S^\ominus$ from the value of Z'_{XY} derived in part (a). Provide an interpretation of the result that you obtain. [7]

Question continues.....

- (c) The formulation of transition-state theory in terms of statistical mechanics can be expressed in a simple way as

$$k_2 = (k_B T/h)(1/c^\ominus)(q''_{\text{TS}}/q'_{\text{REACTANTS}})\exp(-E_c/RT).$$

State what q''_{TS} and $q'_{\text{REACTANTS}}$ are in this equation, and what the double-prime symbol represents. [2]

The quantities q can be factorized into components for translational (q_t), rotational (q_r) and vibrational (q_v) motions where they exist. Conduct this exercise for the available motions (a) for hard-sphere reactants; and (b) for reaction (1) between OH and CHCl_3 . Label the rate constants for the two reactions as k_2^a and k_2^b , and use the combinations of partition functions to give an expression for the ratio k_2^b/k_2^a . [5]

If the average value of $q_r = 30$ and $q_v = 8$ for the reactants and transition state in the OH + CHCl_3 system, calculate the value of k_2^b/k_2^a for reaction (1). Compare this ratio with the value of A/Z'_{XY} that you obtained in the answer to part (a). [4]

Turn over.

12. Molecular Reaction Dynamics

(a) Explain what is meant by (i) *reaction cross section*; (ii) *differential cross section*; and (iii) *angular-scattering distribution function* for a chemical reaction. [3]

(b) The reaction $\text{Cl} + \text{CH}_4$ is said to have a ‘late barrier’ to reaction.

(i) What is the meaning of this statement? [2]

(ii) How might increased vibrational excitation in the CH_4 reactant affect the reactivity for a process with such a barrier? [2]

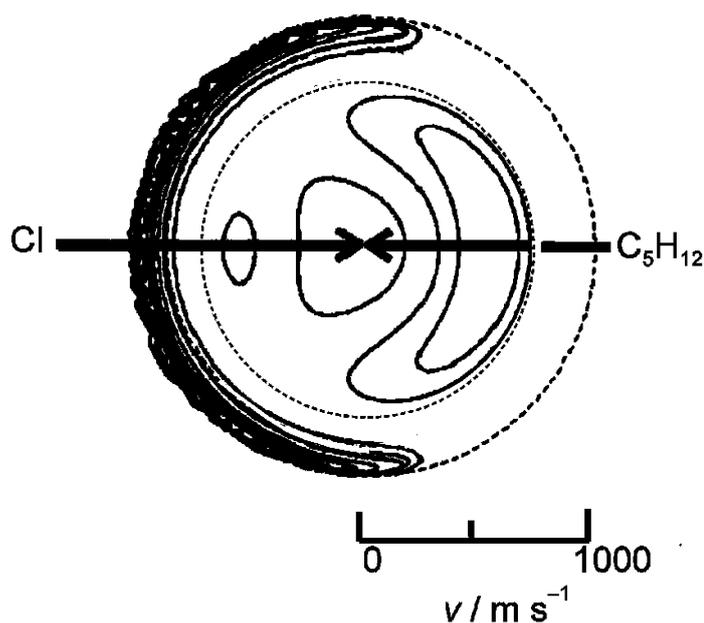
The internuclear separation in $\text{H}-\text{Cl}$ is 0.13 nm, and the $\text{C}-\text{H}$ bond distance in CH_4 is 0.11 nm. For a particular set of reaction conditions, the reaction cross section is found to be 0.011 nm^2 .

(iii) Estimate the hard-sphere collision cross section; [2]

and

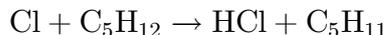
(iv) The apparent steric ‘ P ’ factor. [2]

(c)



Question continues...

The figure shows the velocity-flux contour map for the pentyl (C_5H_{11}) radical obtained in experiments on the reaction of ^{35}Cl atoms with $n\text{-C}_5\text{H}_{12}$ ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)



The dashed circles are guidelines for speeds of 620 m s^{-1} (inner) and 925 m s^{-1} (outer).

- (i) Explain what the coordinates and contours are on this diagram. [2]
- (ii) Discuss in outline the experimental methods by which the data presented in such a diagram might be obtained. [2]
- (iii) The reaction involves abstraction of hydrogen atoms from primary positions to yield 1-pentyl ($1\text{-C}_5\text{H}_{11}$) radicals and from secondary positions to form 2-pentyl ($2\text{-C}_5\text{H}_{11}$) or 3-pentyl radicals ($3\text{-C}_5\text{H}_{11}$). Estimated standard heats of formation $\Delta_f H^\circ$ of the species involved are, in units of kJ mol^{-1} : Cl, 121; HCl, -92 ; $n\text{-C}_5\text{H}_{12}$, -147 ; $1\text{-C}_5\text{H}_{11}$, 61; 2- or $3\text{-C}_5\text{H}_{11}$, 47. 2- and $3\text{-C}_5\text{H}_{11}$ cannot be distinguished from each other in terms of heats of reaction.
Calculate the standard heats of reaction for the abstraction from primary and secondary sites. [3]
- (iv) The figure shows features associated with *forward* and *backward* scattering. What do 'forward' and 'backward' mean in this context? Describe **one** type of reactive encounter in each case that can give rise to the observed behaviour. [3]
- (v) From the maximum speeds of C_5H_{11} observed, estimate roughly (using the speeds given earlier) the maximum energy found in the C_5H_{11} fragments in both the forward and backward scattering (directions are referred to the incoming C_5H_{12} molecules). Show that the total energy release (summed over the C_5H_{11} and HCl products) is about 89 kJ mol^{-1} in one of the cases, and 40 kJ mol^{-1} in the other. [Hint: remember that both momentum and energy are conserved in the fragmentation]. [4]
- (vi) One plausible interpretation of the results obtained is that the forward scattering is associated with abstraction from one type of site, and the backward scattering with the other.

The total relative kinetic energy of the reactants in the experiments to which the figure refers was 70 kJ mol^{-1} . Use the information that you have obtained in the answers to parts (iii) and (v) to identify the processes that give rise predominantly to forward and to backward scattering. [3]

Question continues.....

Turn over.

- (vii) What qualitative conclusions can you now reach about the probability of significant internal excitation in the 1-C₅H₁₁ radicals on the one hand and the 2- and 3-C₅H₁₁ radicals on the other? [2]
- (viii) Quantitative measurement of the distribution of product radicals suggests that 74% are scattered into the forward direction and 26% into the backward direction. Use these data to suggest a relative reactivity for abstraction of primary and secondary hydrogen atoms from *n*-C₅H₁₂. [2]
- Now predict the relative rates of abstraction of H atoms from the primary and secondary sites in propane, assuming that the relative reactivities of the sites are the same in C₃H₈ as in *n*-C₅H₁₂. [2]

End of Examination