

DCHA 2713

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Tuesday, 10th June 2003, 2.20 p.m. to 5.30 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 weight given to each part of the question.

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

1. Vibration-Rotation Spectroscopy
2. Nuclear Magnetic Resonance
3. Valence Theory of H₂
4. Ions in Solution
5. Symmetry and Electronic Spectroscopy
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

DCHA 2713

Turn over

Fundamental Constants

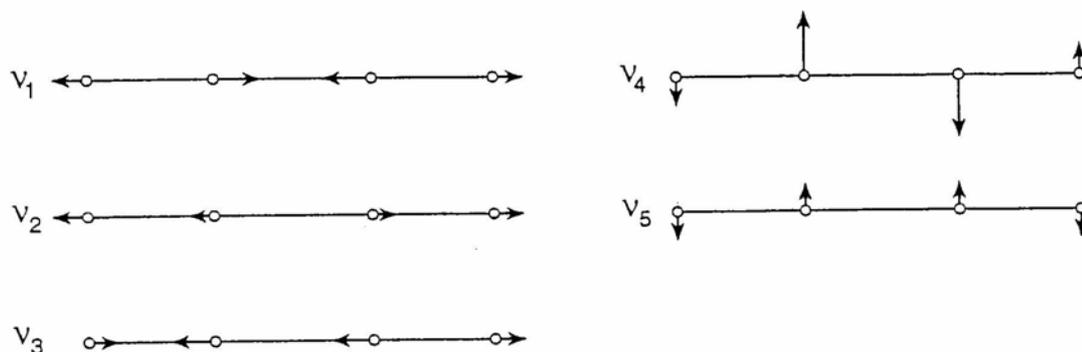
Speed of light	c	$2.997 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	k_B	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	F	$9.649 \times 10^4 \text{ C mol}^{-1}$
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	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

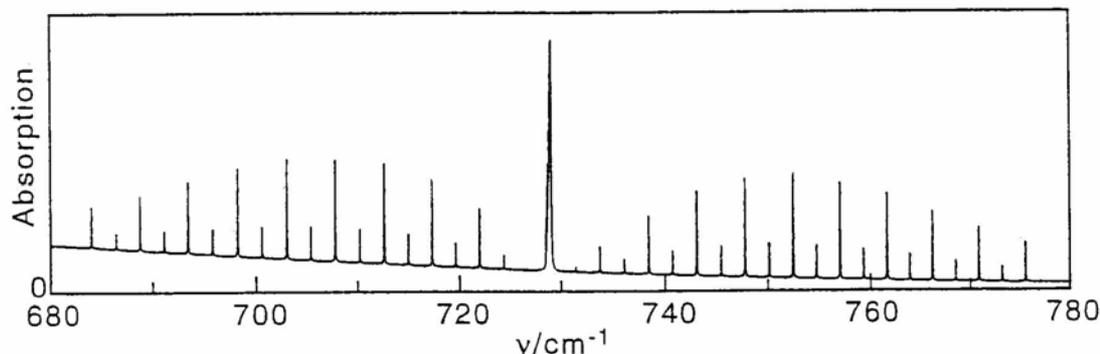
p^\ominus	=	1 bar = 10^5 Pa	1 atm = 101.325 kPa = 760 Torr
m^\ominus	=	1 mol kg^{-1}	1 L = 1 dm^3
1 Da	=	1 g mol^{-1}	1 M = 1 mol L^{-1}

1. Vibration-Rotation Spectroscopy

- (a) Identify the symmetries of the normal vibrations of linear symmetric X_2Y_2 molecules, shown below, and discuss their infra-red and Raman activity. [7]



- (b) Account fully for the appearance of the spectrum shown below, which is a fundamental infra-red absorption band of $^{12}C_2H_2$. What differences would be observed in the corresponding infra-red spectral ranges for $^{12}C_2D_2$ and $^{12}C_2HD$? [8]



- (c) Given that the average spacing between the lines in the above spectrum is 2.352 cm^{-1} , and that the corresponding spacing in $^{12}C_2D_2$ is 1.696 cm^{-1} , estimate the C-C and C-H bond lengths in C_2H_2 . (You may assume that the C-H and C-D bonds have the same length.) [10]

DCHA 2713

Question continues
Turn over

- (d) The first electronically excited state of C_2H_2 is known to be bent. How would this change in structure be reflected in the electronic absorption and emission spectra? To what extent could spectral observations determine the *cis*- or *trans*- conformation in the upper state? [8]

2. Nuclear Magnetic Resonance

Answer **both** part A and part B

Part A.

Discuss the following observations in relation to nuclear magnetic resonance spectroscopy.

- (a) Nuclear magnetic resonance signals are detected in a *strong* permanent *uniform* magnetic field. [3]
- (b) Relaxation processes in proton NMR are *slow*. [3]
- (c) The resolution of proton NMR is much higher than that for nuclei with spin $I \geq 1$. [3]
- (d) The linewidths in solid state NMR, which are much larger than those of liquid samples, can be reduced by *rapid* magic angle spinning. [4]
- (e) Fourier transform NMR signals are excited by a radio frequency pulse with a carefully designed *intensity* and *duration*. [4]
- (f) Inhomogeneous contributions to the transverse relaxation time, T_2 , may be eliminated by spin echo techniques. [4]

Part B

- (a) Given the approximate Hamiltonian for a pair of coupled nuclei with nuclear spin $I = 1/2$,

$$H^{(0)} = \nu_1 I_{1z} + \nu_2 I_{2z} + J I_{1z} I_{2z},$$

which is valid for $\Delta\nu = |\nu_1 - \nu_2| \gg J$, where ν_1 and ν_2 are the two resonance frequencies and J is the coupling constant, determine the energy levels of the system, and show that appropriate selection rules lead to a four-line NMR spectrum. [Hint: consider matrix elements of $H^{(0)}$ in the basis $\alpha_1\alpha_2, \alpha_1\beta_2, \beta_1\alpha_2, \beta_1\beta_2$.] [7]

(b) An additional spin-spin coupling term, $H^{(1)}$, with non-zero matrix elements

$$\langle \alpha_1\beta_2 | H^{(1)} | \beta_1\alpha_2 \rangle = \langle \beta_1\alpha_2 | H^{(1)} | \alpha_1\beta_2 \rangle = \frac{1}{2}J$$

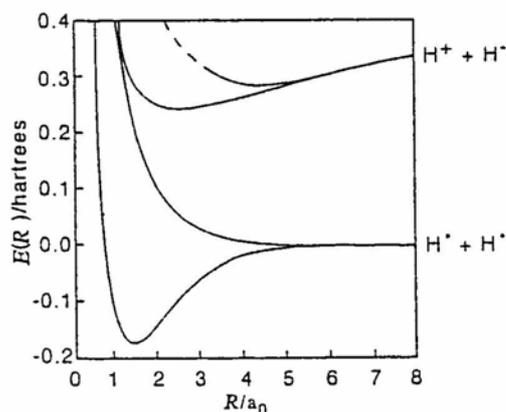
must be added to $H^{(0)}$ if $\Delta\nu \ll J$. Use the full Hamiltonian, $H = H^{(0)} + H^{(1)}$, in conjunction with the triplet and singlet nuclear spin wavefunctions

triplet	singlet
$\alpha_1\alpha_2$	
$\frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \beta_1\alpha_2]$	$\frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \beta_1\alpha_2]$
$\beta_1\beta_2$	

to explain why the spectrum of an A_2 system ($\Delta\nu = 0$) consists of a single line. [5]

3. Valence Theory of H₂

- (a) Outline the molecular orbital theory of binding in H₂⁺ in terms of the Hamiltonian matrix elements $\alpha = \langle a | H | a \rangle = \langle b | H | b \rangle$ and $\beta = \langle a | H | b \rangle = \langle b | H | a \rangle$, where a and b are the two 1s atomic orbitals. Why does the binding energy of H₂ differ from twice that of H₂⁺? [7]
- (b) The potential energy curves for the four electronic states of H₂ involving occupation of 1s orbitals are shown below. The dashed portion of the upper curve indicates interactions with higher electronic states, which are irrelevant to this question.



- (i) The following two electron functions are symmetrized spatial combinations arising from molecular orbital configurations involving the $\sigma_g = (a + b)/\sqrt{2}$ and $\sigma_u = (a - b)/\sqrt{2}$ molecular orbitals:

$$\begin{aligned} \Psi_1 &= \sigma_g(1)\sigma_g(2) \\ \Psi_2 &= \sigma_u(1)\sigma_u(2) \\ \Psi_3 &= [\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)]/\sqrt{2} \\ \Psi_4 &= [\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)]/\sqrt{2} \end{aligned}$$

Determine spatial symmetries and spin-multiplicities for these states. Also suggest assignments to the above potential curves, on the basis of their relative energies. [6]

- (ii) Express Ψ_1 and Ψ_2 in terms of the atomic orbitals a and b . Hence determine their *covalent* and *ionic* characters, and comment on their behaviour at the dissociation limit. [8]

- (iii) It may be shown, in the limit of infinitely separated atoms, that the only non-zero matrix elements of the exact Hamiltonian between the atomic orbitals are given by

$$\begin{aligned}\langle a(1)b(2)|H|a(1)b(2)\rangle &= \langle b(1)a(2)|H|b(1)a(2)\rangle = 2E_{1s} \\ \langle a(1)a(2)|H|a(1)a(2)\rangle &= \langle b(1)b(2)|H|b(1)b(2)\rangle = 2(E_{1s} + X) .\end{aligned}$$

Show that Ψ_1 and Ψ_2 are coupled by a matrix of the form

$$\begin{pmatrix} \langle \Psi_1|H|\Psi_1\rangle & \langle \Psi_1|H|\Psi_2\rangle \\ \langle \Psi_2|H|\Psi_1\rangle & \langle \Psi_2|H|\Psi_2\rangle \end{pmatrix} = \begin{pmatrix} 2E_{1s} + X & -X \\ -X & 2E_{1s} + X \end{pmatrix},$$

and find its eigenvalues.

[8]

- (iv) What properties of the H atom determine the quantity X ?

[4]

4. Ions in Solution

- (a) The chemical potential of a monovalent electrolyte M^+X^- in solution satisfies

$$\mu = \mu^\ominus + 2RT \ln \gamma_\pm (m/m^\ominus)$$

where $\ln \gamma_\pm$ is given by the Debye-Huckel limiting law as

$$\ln \gamma_\pm \simeq -2.303A\sqrt{I}.$$

- (i) Define the term I , the ionic strength, in this equation. [2]

- (ii) Given that A is proportional to $(\epsilon T)^{-3/2}$, where ϵ is the relative permittivity of the solvent and T is the temperature, show that

$$\mu \simeq \mu^{\text{ideal}} - C\sqrt{\frac{I}{\epsilon^3 T}}$$

where C is a positive constant. [3]

- (iii) Use the formula in part (ii) to deduce the circumstances for which the Debye limiting law will be most accurate. [2]

- (b) Use your understanding of the physical basis of Debye-Huckel theory to explain why $\mu - \mu^{\text{ideal}}$ (i) is negative, (ii) increases in magnitude with increasing ionic strength, (iii) decreases in magnitude with increasing solvent permittivity, and (iv) decreases in magnitude with increasing temperature. [6]

- (c) EMF measurements in water and in methanol at 298 K lead to the values of the mean activity coefficient, γ_\pm , of HCl shown in the following table.

	water	methanol
$m = 0.002 m^\ominus$	0.95	0.81
$m = 0.005 m^\ominus$	0.92	0.72
$m = 0.008 m^\ominus$	0.90	0.66

- (i) Show that the Debye-Huckel limiting law is valid for both solvents at these molalities. [4]

(ii) Given that the relative permittivity of water is 78.6 at 298 K, calculate the relative permittivity of methanol. [4]

(iii) The Debye length, λ , which is often taken as a measure of the radius of the *ionic atmosphere* surrounding an ion, is proportional to $(\epsilon/I)^{1/2}$, where ϵ and I are as above. Given that λ is approximately 10 nm in an aqueous solution of monovalent electrolyte M^+X^- of molality $0.001 m^\ominus$, use your result from (c)(ii) to calculate the values of λ for HCl in water and methanol at a molality of $0.008 m^\ominus$. Comment on the results that you obtain. [4]

(d) (i) Why is the Debye length, λ , also an important parameter in theories for the repulsive interaction energy between colloidal particles in electrolyte solutions? [3]

(ii) For two flat plates the repulsive interaction energy per unit area at a constant electrolyte concentration may be written

$$E(d) \propto \exp\left(-\frac{d}{\lambda}\right)$$

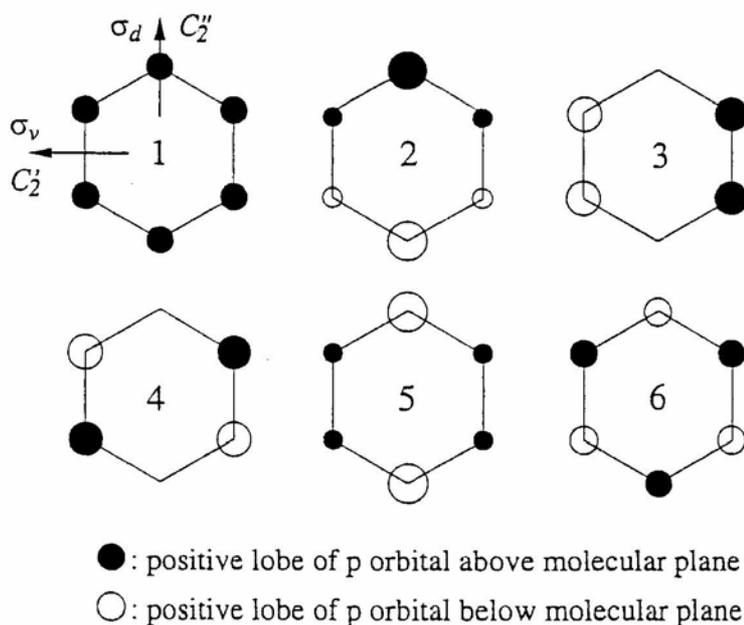
where d is the separation between the plates. For two flat mica plates in an aqueous monovalent electrolyte M^+X^- solution, E was found to vary with distance as follows:

$E/\text{mJ m}^{-2}$	0.1	0.053	0.028	0.015	0.008
d/nm	20	40	60	80	100

Show by graphical means that the interaction energy conforms to the above equation and use your graph and the value of the Debye length from (c)(iii) to calculate the concentration of electrolyte used to make the measurements. [5]

5. Symmetry and Electronic Spectroscopy.

- (a) The π molecular orbitals of benzene are illustrated below. Taking the C_2'' rotational axes and the σ_d dihedral planes to pass through C–H groups, as indicated in the first panel, use the character tables provided to assign symmetry labels to these molecular orbitals. [Hint: Orbitals 2 and 3 form a degenerate pair, as do orbitals 4 and 5, and it suffices to consider the symmetry operations C_2 , i , σ_h and σ_v .] [7]

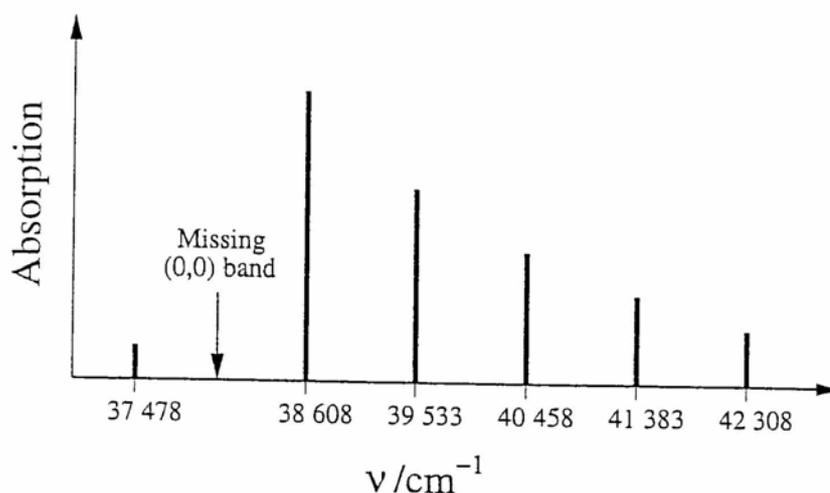


- (b) Hence deduce the term symbols of (i) the ground electronic state of benzene and (ii) all of the electronic states that arise from the first excited electron configuration. Which of these excited states is connected to the ground state by an allowed electronic (electric dipole) transition? [5]
- (c) The \tilde{A} electronic state of benzene has the term symbol ${}^1B_{2u}$. The transition from the ground (\tilde{X}) state to the \tilde{A} state is electronically forbidden, but some vibronic transitions between the two states are allowed. Determine the symmetries of the \tilde{A} vibrational states that induce vibronic transitions from the ground vibrational level of the \tilde{X} state. [7]

(d) The $\tilde{A} \leftarrow \tilde{X}$ absorption spectrum of benzene vapour is sketched below. Given that benzene has

- (i) no b_{1g} symmetry vibrational modes,
- (ii) an a_{1g} symmetry C–C stretching vibration (denoted ν_2) with a frequency of 993 cm^{-1} in the \tilde{X} state, and
- (iii) an e_{2g} symmetry C–C–C bending vibration (denoted ν_{18}) with a frequency of 608 cm^{-1} in the \tilde{X} state,

suggest an assignment for the vibrational transitions in this spectrum. Also determine the ν'_2 and ν'_{18} vibrational frequencies in the \tilde{A} electronic state, and comment on the values you obtain. [8]

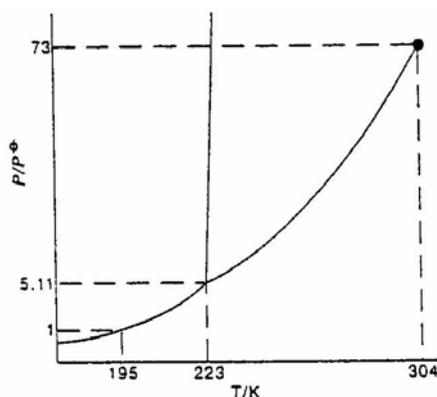


(e) Use your assignment to explain the following experimental observations concerning the vapour, liquid and solid-state ultra-violet spectra of benzene. [6]

- (i) In the vapour phase, the intensity of the vibronic absorption band at $37\,478 \text{ cm}^{-1}$ increases with increasing temperature.
- (ii) The band with the shortest wavelength in the $\tilde{A} \rightarrow \tilde{X}$ fluorescence spectrum of liquid benzene is centred on $37\,478 \text{ cm}^{-1}$.
- (iii) An additional broad band centred on $38\,086 \text{ cm}^{-1}$ is seen in the spectrum of solid benzene at low temperatures.

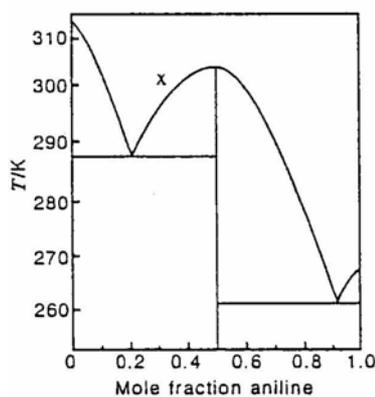
6. Thermodynamics

(a)



- (i) Label the areas in the above phase diagram of CO_2 . (The dashed lines simply indicate the scale.) [3]
- (ii) Sketch and explain the variation of the chemical potential of the stable phase as the temperature is increased from 200 K to 300 K at $p/p^\ominus = 50$. [4]
- (iii) Sketch and explain the variation of pressure with volume throughout the range of the diagram along isotherms at $T = 250$ K, 300 K and 350 K. [4]

(b)



An equimolar solution of phenol (A) in aniline (B) crystallizes as a definite compound AB. As a consequence, the above temperature composition diagram can be interpreted as a combination of two eutectic diagrams - one for (A,AB) and one for (AB,B).

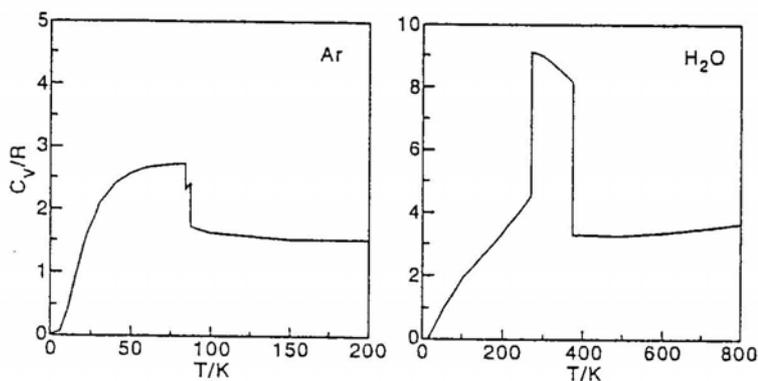
(i) Estimate the melting points of A, B and AB. [2]

(ii) Label the areas in the diagram, and show that the divisions are consistent with the phase rule, $P + F = C + 2$. [3]

(iii) Discuss the behaviour of the system when material at the point x is allowed to cool to 280 K. Include a description of the temperature variation with time. [4]

(iv) What changes would occur as aniline is progressively added to material at the point x , while the temperature is held constant? [3]

(c)



Account for the heat capacity variations of solid and gaseous Ar and H₂O shown above. (You need not discuss the behaviour of the heat capacities of the liquids.)

[10]

7. Quantum Mechanics.

- (a) Find the value of the constant α for which the wavefunction $\psi_0(x) = N_0 e^{-\alpha x^2/2}$ is an eigenfunction of the harmonic oscillator Hamiltonian

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2,$$

and determine the corresponding energy eigenvalue. (Note that you are **not** required to calculate the normalization constant N_0 .) [8]

- (b) Show that the wavefunction $\psi_1(x) = N_1 x e^{-\alpha x^2/2}$ is also an eigenfunction of the oscillator Hamiltonian, and determine its energy eigenvalue. (You need not determine the normalization constant N_1 .) Explain why $\psi_0(x)$ must be the ground and $\psi_1(x)$ the first excited state of the oscillator, and show that the two wavefunctions are orthogonal. [9]

- (c) The Hamiltonian for the degenerate bending vibration of a linear triatomic molecule is

$$H = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} k (x^2 + y^2),$$

where the coordinates x and y are proportional to perpendicular displacements of the central atom from the molecular axis. Write down the three lowest eigenfunctions of this Hamiltonian and the corresponding energy eigenvalues. [4]

- (d) Show that if two wavefunctions $\Psi_{1,0}$ and $\Psi_{0,1}$ are degenerate eigenfunctions of a Hamiltonian H with eigenvalue E then the linear combinations $\Psi_{1,\pm} = \sqrt{1/2}(\Psi_{1,0} \pm i\Psi_{0,1})$ are also eigenfunctions of H with the same energy eigenvalue. Show further that if $\Psi_{1,0}$ and $\Psi_{0,1}$ are orthonormal then so are $\Psi_{1,+}$ and $\Psi_{1,-}$. [5]

- (e) Hence show that the lowest three eigenfunctions of the Hamiltonian in part (c) can be specified equivalently as

$$\Psi_{0,0}(r, \phi) = N_0^2 e^{-\alpha r^2/2}$$

and

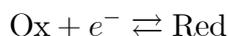
$$\Psi_{1,\pm}(r, \phi) = \sqrt{1/2} N_0 N_1 r e^{-\alpha r^2/2} e^{\pm i\phi},$$

where r and ϕ are polar coordinates such that $x = r \cos \phi$ and $y = r \sin \phi$. [3]

- (f) The operator for the projection of the vibrational angular momentum on the molecular axis is $L_z = -i\hbar\partial/\partial\phi$. Show that the wavefunctions $\Psi_{0,0}(r, \phi)$ and $\Psi_{1,\pm}(r, \phi)$ are eigenfunctions of this operator, and determine the corresponding angular momentum eigenvalues. What do your results imply about the rotational structure that will be seen in the vibrational (IR) spectrum of a linear triatomic molecule? [4]

8. Interfacial Kinetics

(a) For the electrode reaction

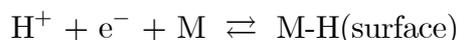


the net current, i , depends on the applied potential, $\eta = E - E^\ominus$, as

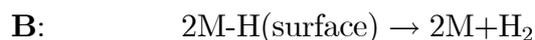
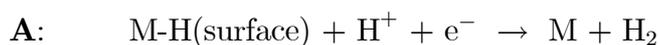
$$i \propto \left\{ -k_1 [\text{Ox}] \exp\left(-\frac{\alpha F \eta}{RT}\right) + k_2 [\text{Red}] \exp\left(\frac{\beta F \eta}{RT}\right) \right\}$$

Explain the meaning of the various terms in this equation. [5]

(b) It has been proposed that **Step 1** in the reduction of H^+ in acidic solution at a metal electrode is



Step 2 in the proposed mechanism may be either **A** or **B** below:



(i) Write an expression for the current in the situation when only the forward reaction in **Step 1** is significant. [3]

(ii) When either **A** or **B** is rate determining, **Step 1** may be treated as an equilibrium. In this case, by assuming that the forward and backward rates of **Step 1** are equal, and that the transfer coefficients are 1/2, show that the isotherm for the initial adsorption (*i.e.* **Step 1**) is

$$\frac{\theta}{1 - \theta} = K[\text{H}^+] \exp\left(-\frac{F}{RT}\eta\right)$$

where K is a constant and θ is the coverage. [6]

- (iii) Close to the equilibrium potential the term on the right hand side of the equation in (b)(ii) is small in comparison with unity and hence $(1 - \theta) \simeq 1$. Use this approximation to write expressions for the overall rate of the reaction when **A** and **B** are rate determining and hence show that the currents in the two cases are respectively (taking the transfer coefficient in **A** to be 1/2)

$$\mathbf{A}: \quad i \propto [\text{H}^+]^2 \exp\left(-\frac{3F}{2RT}\eta\right)$$

and

$$\mathbf{B}: \quad i \propto [\text{H}^+]^2 \exp\left(-\frac{2F}{RT}\eta\right). \quad [7]$$

- (iv) The following $i - \eta$ data for the evolution of hydrogen on a metal at 300 K have been obtained:

$i/\text{A cm}^{-2}$	-10^{-4}	-5×10^{-4}	-2.5×10^{-3}	-10^{-2}
η/V	-0.010	-0.031	-0.052	-0.070

Which of the three possible mechanisms above account best for this behaviour?
Take RT/F to be 0.0258 V. [7]

- (c) The standard exchange current densities for the hydrogen evolution reaction in 1 mol dm^{-3} acid and the strengths, E_{MH} , of the corresponding M-H bonds are given for a number of metals in the table below. To what extent are these data qualitatively consistent with the mechanism in part (b)? [5]

metal	Zn	Ni	Pt	W	Ti
$i_0/\text{A cm}^{-2}$	10^{-10}	3×10^{-8}	3×10^{-5}	10^{-9}	10^{-11}
$E_{MH}/\text{kJ mol}^{-1}$	8	12	15	18	20

9. Statistical Mechanics

- (a) Indicate how the equation

$$A = -kT \ln Q$$

may be used to relate thermodynamic properties to quantum mechanical energy levels. How is Q related to the *molecular partition function*, q , for a system of non-interacting particles? [5]

- (b) Derive an expression for q in the case of an oscillator, with energy levels $\epsilon_n = nh\nu$. Hence show that the mean energy per oscillator is given by

$$u = \frac{h\nu}{e^{h\nu/kT} - 1}. \quad [7]$$

[Hint: It may be assumed that $1 + x + x^2 \dots = (1 - x)^{-1}$ for $x < 1$.]

- (c) The Einstein theory of black-body radiation requires a knowledge of the number, $N(\nu)$, of photon modes with frequency less than or equal to ν in a cavity of volume V , which is given by

$$N(\nu) = \frac{8\pi V\nu^3}{3c^3}.$$

Derive an expression for the number, $P(\nu)d\nu$, of modes per unit volume with frequencies between ν and $\nu + d\nu$. [3]

- (d) Hence show that, for radiation in equilibrium with a black body at temperature T , the energy density, $\rho(\nu)$, of the radiation, per unit frequency, is given by

$$\rho(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}. \quad [3]$$

- (e) Obtain expressions for $\rho(\nu)$ in the limits $(h\nu/kT) \gg 1$ and $(h\nu/kT) \ll 1$, sketch the function $\rho(\nu)$, and comment on its significance for the origin of the quantum theory.

[7]

- (f) The Einstein theory of spectroscopic transitions between species X and X*, at frequency ν , is based on two assumptions. The rate of stimulated absorption, $B(\nu)\rho(\nu)[X]$, is assumed to match the combined rates of stimulated and spontaneous emission, $[B(\nu)\rho(\nu) + A(\nu)][X^*]$. In addition X and X* are taken to be in thermal equilibrium. Show that

$$A(\nu) = \frac{8\pi h\nu^3}{c^3} B(\nu). \quad [8]$$

10. Atomic Spectroscopy.

- (a) State the selection rules that apply to atomic electric dipole transitions within the Russell-Saunders (LS) coupling approximation. [4]
- (b) All of the microstates with $M_L \geq 0$ and $M_S > 0$ that are compatible with the Pauli exclusion principle for the ground $1s^2 2s^2 2p^3$ electron configuration of the nitrogen atom are given in the following table. Deduce the term symbols that arise from this electron configuration. [4]

	$M_S = 3/2$	$M_S = 1/2$
$M_L = 2$		$\uparrow\downarrow$ \uparrow \square
$M_L = 1$		\uparrow $\uparrow\downarrow$ \square $\uparrow\downarrow$ \square \uparrow
$M_L = 0$	\uparrow \uparrow \uparrow	\uparrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow

Notation: $m_l = \begin{matrix} \square & \square & \square \\ 1 & 0 & -1 \end{matrix}; \quad m_s = \begin{matrix} \uparrow & \downarrow \\ 1/2 & -1/2 \end{matrix}$

- (c) Determine the term symbols that arise from the $1s^2 2s^2 2p^2$ electron configuration of the carbon atom, and use this information to deduce the term symbols that arise from the excited $1s^2 2s^2 2p^2 3s^1$ and $1s^2 2s^1 2p^4$ electron configurations of the nitrogen atom. [8]
- (d) The wavenumbers of the first six fully allowed transitions in the absorption spectrum of atomic nitrogen are given on the next page. Deduce as much as you can about the electronic states involved in these transitions. [Hint: The Lande interval rule is that, for a given L and S , the energy difference between two neighbouring levels, J and $J + 1$, is proportional to $J + 1$.] [9]

Transition	Wavenumber (cm ⁻¹)
1	83284
2	83318
3	83365
4	88107
5	88151
6	88171

- (e) When each of these six transitions is examined under higher resolution it splits into a closely-spaced multiplet as a result of the hyperfine interaction. Explain why the hyperfine splitting in the ground electronic state can be ignored, and use this fact to predict the number of hyperfine components in each transition. [The ¹⁴N nucleus has $I = 1$.] [8]

11. Theories of Kinetics.

- (a) Discuss the physical interpretation of the symbols σ , \bar{c} and E_0 in the simple collision theory expression for the rate coefficient of a bimolecular reaction,

$$k(T) = P\sigma\bar{c}e^{-E_0/RT}. \quad [3]$$

- (b) Simple collision theory does not provide a prescription for the steric factor P . However, P can be estimated in quite a straightforward way for reactions such as $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$, which proceed via the harpoon mechanism. Describe what this mechanism entails and, given that the Coulomb potential between two charges q_1 and q_2 separated by a distance r is

$$V(r) = \frac{q_1q_2}{4\pi\epsilon_0r},$$

show that it leads to a reaction cross section of the form

$$\sigma = \pi \left[\frac{e^2}{4\pi\epsilon_0(I_{\text{K}} - E_{\text{Br}_2})} \right]^2,$$

where I_{K} is the ionisation energy of K and E_{Br_2} is electron affinity of Br_2 . By comparing this expression with the simple collision theory expression for σ , calculate P for the $\text{K} + \text{Br}_2$ reaction given that $I_{\text{K}} = 4.3$ eV, $E_{\text{Br}_2} = 1.2$ eV and the sum of the covalent radii of K and Br_2 is 0.4 nm. Comment on the result you obtain. [9]

- (c) More generally, P can be calculated using transition state theory, which gives the rate coefficient of a bimolecular reaction $\text{A} + \text{B} \rightarrow \text{products}$ as

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

State the physical assumptions that lead to this expression, and provide one example of a situation where these assumptions might be expected to break down. [5]

- (d) Given that q_{\ddagger} , q_{A} and q_{B} are molecular partition functions per unit volume, the translational contributions to which can be written as (e.g.)

$$q_{\text{A,trans}} = \left(2\pi m_{\text{A}} k_{\text{B}} T / h^2 \right)^{3/2},$$

show that in the hypothetical case of a reaction between two hard spheres the transition state theory rate coefficient reduces to the simple collision theory result with $P = 1$, $E_0 = \Delta E_0^{\ddagger}$, and

$$\bar{c} = \left(\frac{8(m_{\text{A}} + m_{\text{B}})k_{\text{B}}T}{\pi m_{\text{A}}m_{\text{B}}} \right)^{1/2}. \quad [8]$$

**Question continues
Turn over**

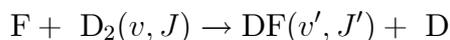
- (e) Hence deduce that the steric factor for a reaction between two molecules A and B that proceeds via a linear transition state is given by

$$P \simeq \frac{q'_{\ddagger}}{q'_A q'_B},$$

where the translational contributions are absent from the primed partition functions q'_{\ddagger} , q'_A and q'_B and the rotational contribution is also absent from q'_{\ddagger} . Noting that $q_{\text{vib}} \simeq 1$ per vibrational degree of freedom and $q_{\text{rot}} \simeq 10$ per rotational degree of freedom at room temperature, estimate the steric factor for (i) a reaction between an atom and a diatomic molecule, and (ii) a reaction between two diatomic molecules, assuming that the transition state is linear in both cases. Comment on the results you obtain. [8]

12. Molecular Reaction Dynamics

(a) The reaction



with $v = J = 0$, has a reaction cross-section, $\sigma = 0.05 \text{ nm}^2$ at an initial relative translational energy, $\bar{E}_T = 13.5 \text{ kJ mol}^{-1}$.

(i) Use data from the following table to determine the total available energy of the products relative to the zero point level. [4]

Species	$\bar{\nu}/\text{cm}^{-1}$	B/cm^{-1}	$D_0/\text{kJ mol}^{-1}$
D ₂	2991	30.5	439
DF	2906	11.0	573

(ii) The rotational energy distributions of different product vibrational levels are found to peak at an energy roughly equal to half the vibrational energy separation. Estimate the angular momentum, J' , in the product rotation. [4]

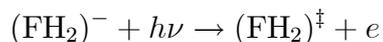
(iii) The distribution over product vibrational states is found to peak at $v' = 3$. Estimate the values of E_{trans} , E_{rot} and E_{vib} at this peak and comment on any implications about the form of the potential energy surface. [5]

(iv) The maximum angular momentum available to the reacting system may be estimated from the cross-section by use of the equations

$$l_{\max} \hbar = \mu v b_{\max} \quad \text{and} \quad \sigma = \pi b_{\max}^2,$$

where μ is the reduced mass of F relative to D₂ and v is the reactant relative speed. Explain the significance of the quantity b_{\max} . Estimate l_{\max} , and hence deduce an upper bound on the cross-section for the reverse reaction, from $v' = J' = 0$, at the same total energy. [10]

- (b) The negative ion $(\text{FH}_2)^-$ is known to have an $\text{F}\dots\text{H}_2$ separation close to that of the saddle point on the neutral $\text{F} + \text{H}_2$ potential energy surface. Analysis of the photoelectron spectrum, arising from the process



reveals three peaks in the electron kinetic energy distribution attributable to the *ortho* $(\text{FH}_2)^\ddagger$ species, with spacings of 403 cm^{-1} and 1032 cm^{-1} . A separate experiment, starting with *para* $(\text{FH}_2)^-$ gave peaks separated by 565 cm^{-1} and 782 cm^{-1} . From the information given in part (a)(i), calculate the rotational constant, B , for H_2 and hence examine the proposal that the H_2 is freely rotating in the transition state, $(\text{FH})_2^\ddagger$. [10]

[$1 \text{ kJmol}^{-1} \cong 83.6 \text{ cm}^{-1}$. Relative atomic masses $\text{F} : 19, \text{D} : 2$]