

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Wednesday, 14<sup>th</sup> June 2000, 9.30 a.m. - 12.40 p.m.

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*Answer **THREE** 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.

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1. Thermodynamics
2. Valence
3. Molecular Spectroscopy
4. Surfaces and Interfacial Reactions
5. Atomic Spectroscopy
6. Nuclear Magnetic Resonance
7. Statistical Mechanics and Surfaces
8. Chemical Reaction Rates and Reaction Dynamics
9. Quantum Mechanics
10. Photochemistry
11. Atmospheric Chemistry
12. Molecular Interactions
13. Physical Chemistry of Elemental and Combined Hydrogen

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

## 1. Thermodynamics

- (a) State the third law of thermodynamics. [2]
- (b) What is meant by the *third law entropy* of a substance, and how can this quantity be determined for a gaseous substance from experimental data? [5]
- (c) What is the *statistical entropy*? Outline briefly how it can be determined from theoretical or experimental (spectroscopic) information. [5]
- (d) Explain why the heat capacities of polyatomic gases are functions of temperature. [4]
- (e) The constant pressure heat capacity  $C_p$  of  $\text{CO}_2(\text{g})$  follows the equation

$$C_p = 44.2 + 8.79 \times 10^{-3}T - 8.54 \times 10^5/T^2$$

where  $C_p$  is expressed in  $\text{J K}^{-1} \text{mol}^{-1}$  and  $T$  is in K. Low temperature measurements give the third law entropy of solid  $\text{CO}_2$  at its sublimation temperature, 194.6 K, as  $70.8 \text{ J K}^{-1} \text{mol}^{-1}$ . Its enthalpy of sublimation is  $25.23 \text{ kJ mol}^{-1}$ .

Calculate the third law entropy of  $\text{CO}_2(\text{g})$  at 298 K and compare it with the statistical entropy of  $213.7 \text{ J K}^{-1} \text{mol}^{-1}$ . [6]

- (f) The difference between the third law entropy and the statistical entropy is called *residual entropy*. Comment on, and where possible suggest explanations for the following residual entropies (given in  $\text{J K}^{-1} \text{mol}^{-1}$ ):

$$\text{CH}_3\text{D} \quad 11.6 \quad \text{CO} \quad 5.0 \quad \text{H}_2\text{O} \quad 3.4$$

[Note that exact agreement with theory is not expected.] [6]

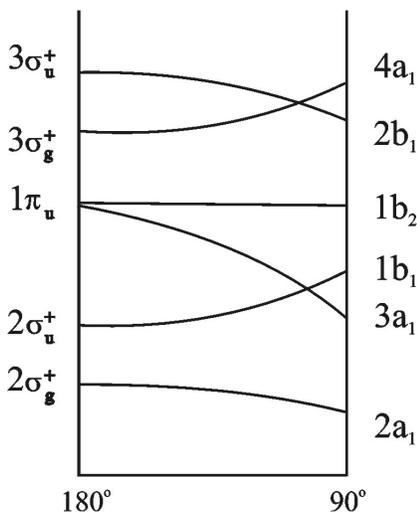
- (g) The entropies of  $\text{H}_2(\text{g})$  and  $\text{HD}(\text{g})$  at 298 K are, respectively,  $130.68 \text{ J K}^{-1} \text{mol}^{-1}$  and  $143.80 \text{ J K}^{-1} \text{mol}^{-1}$ . Account for the *difference* between the two values.

$$\left[ q_{\text{trans}} = \frac{V}{\Lambda^3}, \quad \Lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}, \quad q_{\text{rot}} = \frac{k_B T}{\sigma B} \right]$$

[6]

2. Valence

- (a) What is a *molecular orbital*? What do you understand by the orbital approximation, and why is it useful in quantum mechanics? [4]
- (b) Discuss FIVE of the following. All parts carry equal weight.
- The Walsh diagram for an AH<sub>2</sub> molecule shown below (where A is in second row of the periodic table)



can be used to explain why BeH<sub>2</sub> is linear in its ground electronic state, but H<sub>2</sub>O is bent. It also helps to rationalize why several of the excited electronic states of water, and of the water ion H<sub>2</sub>O<sup>+</sup>, have very different equilibrium bond angles from the ground state.

- The ground electronic state of NO is split by spin-orbit coupling, and each spin-orbit state is two-fold degenerate. An electronic transition in NO from the ground electronic state to the A<sup>2</sup>Σ<sup>+</sup> state shows pronounced P, Q and R branches.
- Hückel theory predicts the cyclo-propenium cation, C<sub>3</sub>H<sub>3</sub><sup>+</sup>, to have a resonance stabilization energy of 2β.  
 [ Note that  $(\alpha - E)^3 - 3\beta^2(\alpha - E) + 2\beta^3$  may be factorized  $(\alpha - \beta - E)(\alpha - \beta - E)(\alpha + 2\beta - E)$  ]
- The wavelength of maximum absorption in the π → π\* transitions of conjugated linear alkenes (such as butadiene and hexatriene) *increases* with the number of carbon atoms in the chain.

- v.  $C_2$  has a  $^1\Sigma_g^+$  ground state, and a very low lying excited state of  $^3\Pi_u$  symmetry.
- vi. Within the orbital approximation,  $He_2$  is predicted to be unbound, whereas in reality it has a binding energy of about  $8\text{ cm}^{-1}$ . In spite of the zero bond order predicted by simple molecular orbital theory,  $Be_2$  has a binding energy of  $750\text{ cm}^{-1}$ .
- vii. The gas phase photoelectron spectrum of HCl in the region corresponding to excitation to the first excited  $A^2\Sigma^+$  electronic state of  $HCl^+$  shows a long progression of vibrational bands. These show sharp rotational structure for vibrational levels  $v' < 8$ , and diffuse, broadened structure for levels in the range  $8 \leq v' \leq 10$ . If  $HCl^+$  is excited to levels  $v' > 10$  in the A state, the sharp rotational structure returns.

[30]

### 3. *Molecular Spectroscopy*

- (a) Determine the possible numbers of vibrational degrees of freedom in a tetra-atomic molecule. Why does this number depend on the structure of the molecule? [3]
- (b) Five fundamental vibration bands are found in the infrared (IR) and Raman (R) spectra of an  $X_2H_2$  molecule, as follows:

$$3374 \text{ cm}^{-1} \quad (\text{R})$$

$$3287 \text{ cm}^{-1} \quad (\text{IR})$$

$$1974 \text{ cm}^{-1} \quad (\text{R})$$

$$729 \text{ cm}^{-1} \quad (\text{IR})$$

$$612 \text{ cm}^{-1} \quad (\text{R}).$$

- i. What can be deduced about the molecular structure from the fact that no line is both R and IR active? [2]
- ii. Given that the molecule is  $C_2H_2$ , identify the type of each vibration as C–H or C–C bond stretch, or bend. [5]
- iii. By consideration of the R and IR activity, and the frequencies, assign a symmetry to each mode.  
[A full normal mode analysis is not required.] [5]
- iv. Sketch the form of the atomic displacements in each mode. [5]
- (c) Sketch the appearance of the rotational structure that you would expect to see in
- i. the IR band at  $729 \text{ cm}^{-1}$
- ii. the Raman band at  $3374 \text{ cm}^{-1}$ .

given that the most populated level at room temperature is  $J_{\text{max}} = 9$  [8]

- (d) The equilibrium rotational constants,  $B_e$ , of the molecules  $C_2H_2$  and  $C_2D_2$  are  $1.188 \text{ cm}^{-1}$  and  $0.8556 \text{ cm}^{-1}$  respectively. Determine the C–C and C–H(D) bond lengths, assuming that they are not affected by isotopic substitution. [6]  
[You may use the conversion  $B(\text{cm}^{-1}) = 16.857/I(\text{u } \text{Å}^2)$  and take the hydrogen isotopic masses to be 1.0 u and 2.0 u exactly. ]

#### 4. Surfaces and Interfacial Kinetics

Answer Part **A** and **either** Part **B** or Part **C**. Candidates should note that a sheet containing lattice structures is available for use as a template in Part **B**.

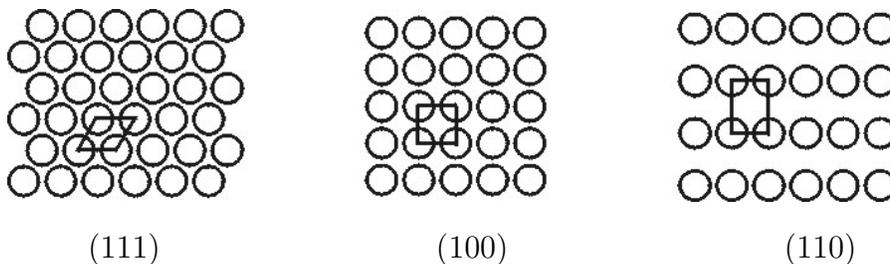
##### A

Scanning probe microscopy is one of the most widely used approaches to the study of surfaces.

- (a) Explain the physical principles behind each of the following techniques and describe how the experiments are conducted:
  - i. scanning tunneling microscopy (STM); [4]
  - ii. atomic force microscopy (AFM). [4]
- (b) Describe the types of information on the structure and/or reactivity of solid surfaces that can be revealed by STM and AFM. (You may draw your examples from surfaces in solution or in ultrahigh vacuum.) [4]
- (c) Contrast the information yielded by scanning probe microscopy with that obtainable by other scattering and spectroscopic techniques. [5]

##### B

The structures of three low Miller index faces of Pt are shown below together with the primitive unit cell on each face.



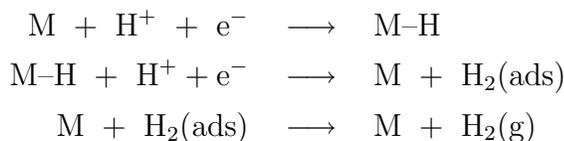
- (a) Clean Pt(110) reconstructs to a  $(1 \times 2)$  surface in which every second row in the topmost layer of atoms is missing. Sketch the LEED patterns expected for the unreconstructed and reconstructed surfaces and suggest a reason why this reconstruction occurs. [5]
- (b) Exposure of the unreconstructed Pt(100) surface to small amounts of CO gives rise to a  $c(2 \times 2)$  overlayer, as determined by LEED (i.e. a  $(2 \times 2)$  overlayer with an extra CO molecule at the centre of each  $(2 \times 2)$  unit cell:  $c(2 \times 2)$  is also known as  $(\sqrt{2} \times \sqrt{2})R45^\circ$ ).

Propose a structure for this surface that is consistent with the LEED pattern and determine the coverage,  $\theta$ , where  $\theta$  is defined as the average number of CO molecules per Pt atom in the topmost layer. What other information is required to distinguish between the various possible structures of the overlayer? [5]

- (c) Exposure of unreconstructed Pt(111) to CO gives rise first to a LEED pattern characteristic of a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  overlayer. Reflection absorption infrared spectroscopy (RAIRS) reveals a single peak at  $2100 \text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) measurements of the O(1s) peak yield a coverage  $\theta = 0.33$ . Increased exposure to CO results in a LEED pattern characteristic of a  $c(2 \times 4)$  overlayer. RAIRS shows two peaks at  $1857 \text{ cm}^{-1}$  and  $2110 \text{ cm}^{-1}$  and XPS establishes the surface coverage to be  $\theta = 0.5$ . Suggest structures for the surface at both these coverages. [7]

## C

- (a) Discuss factors that determine the rate constants of electrochemical reactions at electrode surfaces. [8]
- (b) A proposed mechanism for the hydrogen evolution reaction,  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ , at the surface of a metal, M, is given below:



With the aid of this mechanism, or otherwise, explain why the exchange current density for the reduction of  $\text{H}^+$  on a bright Pt electrode is nine orders of magnitude higher than on a Hg electrode and five orders of magnitude higher than on a Ta electrode. [4]

- (c) Rationalize the heterogeneous rate constants for the one-electron reduction of the following transition metal ions in aqueous solutions.

	$k_0/\text{m s}^{-1}$
$\text{Ru}(\text{NH}_3)_6^{3+}$	$10^{-2}$
$\text{V}^{3+}$	$4 \times 10^{-5}$
$\text{Co}(\text{NH}_3)_6^{3+}$	$5 \times 10^{-10}$

[5]

5. *Atomic spectra*

- (a) The lowest energy atomic absorption line of  $\text{He}^+$  ions is at a photon energy of 40.814 eV, while that of atomic H atoms is at 10.197 eV.
- Give the configurations and term symbols for the states involved in the transitions. [2]
  - Explain why the ratio of photon energies is very close to four. [2]
  - Explain why the ratio is not exactly four. [2]
- (b) At very high resolution the  $\text{He}^+$  line at 40.814 eV is found to be a doublet, with a splitting of 0.0007 eV.
- Explain why the line is split. [2]
  - Estimate the splitting of the line at 10.197 eV in the spectrum of atomic H. [3]
- (c) The first absorption line in the spectrum of *neutral* He is at a photon energy of 21.217 eV.
- Give the configurations and term symbols for the states involved. [2]
  - Suggest reasons why the measured width of this line as seen in emission depends on the pressure and temperature of He gas in a lamp from which it is emitted. [4]
  - Explain why this He emission line splits into three components when a strong magnetic field is applied to its source, whereas the  $\text{He}^+$  doublet line at 40.814 eV splits into a larger number of components. [6]
- (d) The 21.217 eV line of He is the first member of a Rydberg series, with the following photon energies:

Quantum number $n$	2	3	4	5
Energy $E_n/\text{eV}$	21.217	23.086	23.742	24.045

Using the Rydberg formula  $E_n = I - \mathcal{R}/(n - \delta)^2$  where  $I$  is the ionization energy and  $\delta$  is the quantum defect;

- Show that for  $\delta \ll 1$

$$(E_{n+1} - E_n)/\mathcal{R} \simeq \frac{1}{n^2} - \frac{1}{(n+1)^2} + 2\delta \left[ \frac{1}{n^3} - \frac{1}{(n+1)^3} \right]$$

[Recall that for  $x \ll 1$ ,  $1/(1-x)^m \simeq 1 + mx$ .] [5]

- ii. Use the first two energies and the result above to estimate the quantum defect. [3]
- iii. Hence estimate the ionization potential of He as accurately as possible from the data given. [3]

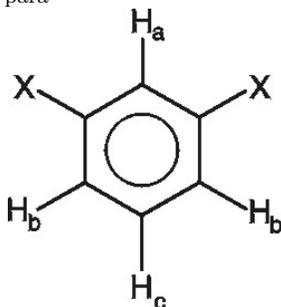
[Hint: the Rydberg constant,  $\mathcal{R}$ , can be obtained from the data given in part (a). No graph or recursive (iterative) calculation is required. ]

## 6. Nuclear Magnetic Resonance

Answer ALL parts.

### A Spin-spin coupling

- (a) Consider a dilute solution of the aromatic molecule shown below in which X is an electron withdrawing group that is not magnetically coupled to the ring protons (e.g., X = Cl). Sketch the  $^1\text{H}$  NMR spectrum if the coupling constants are in the order  $J_{\text{ortho}} \gg J_{\text{meta}} \gg J_{\text{para}}$ .



[Assume that the weak coupling limit applies.] [6]

- (b) Explain qualitatively how the spectrum would change if
- the electron withdrawing groups, X, were magnetically coupled to the ring protons (e.g., X = F),
  - one of the X substituents were replaced by a different non-coupled electron-withdrawing group, Y (e.g., Y = Br).

[Note: In part (b) you are not expected to draw the NMR spectra.] [6]

### B Spin relaxation

- (a) What is meant by *spin-lattice relaxation* and *spin-spin relaxation* in NMR? Describe the most important physical processes that give rise to each type of relaxation in solution. [6]
- (b) Explain the principles behind an experiment to measure
- the spin-lattice relaxation time,  $T_1$
  - the spin-spin relaxation time,  $T_2$
- [5]
- (c) What are the experimental consequences of
- a very long  $T_1$
  - a very short  $T_1$

[4]

- (d) An inversion recovery experiment was conducted to determine the value of  $T_1$  for the methyl carbons in 1,2-dimethyl benzene. The intensity of the  $^{13}\text{C}$  NMR signal is given below as a function of the pulse delay,  $\tau$ .  $I(\infty)$  is the fully relaxed NMR intensity for  $\tau \gg T_1$ .

$\tau/\text{s}$	0	5	10	15	20	25
$I(\tau)/I(\infty)$	-1.0	-0.32	0.13	0.43	0.62	0.75

Use a graphical procedure to calculate  $T_1$  for the methyl carbons in 1,2-dimethyl benzene.

[ Hint: the  $z$ -magnetisation in an inversion recovery experiment recovers as

$$M_z(\tau) = M_z(\infty) (1 - 2e^{-\tau/T_1}) . ]$$

[7]

7. *Statistical Mechanics and Surfaces*

- (a) Derive the following expression for the translational partition function of an atom of mass  $m$  free to move in three dimensions (3d) in a box of volume  $V$ ,

$$q_{3d} = \frac{V}{\Lambda^3} \quad \Lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}.$$

State any assumptions you make. [6]

[ You may use the fact that

$$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$$

and that the energy levels of a particle confined to a one-dimensional box of length  $l$  can be written

$$E_n = \frac{n^2 h^2}{8ml^2} \quad n = 1, 2, 3 \dots ]$$

- (b) For an ideal gas containing  $N_g$  such atoms the canonical partition function may be written

$$Q = \frac{q_{3d}^{N_g}}{N_g!}.$$

(The atoms have been assumed to be occupying only their ground singlet electronic states, and any effects due to nuclear spin have been neglected.)

Under what conditions will Maxwell-Boltzmann statistics be applicable to such a system? Use the expression to show that the Helmholtz free energy of the ideal gas can be written approximately for large  $N_g$

$$A_g - A_g(0) = -N_g k_B T \left[ \ln \left( \frac{q_{3d}}{N_g} \right) + 1 \right]$$

where  $A_g(0)$  is the free energy of the gas atoms at 0 K. Account for the dependence of  $A_g$  on the volume of the container  $V$ . [8]

[ Stirling's approximation can be written  $\ln N! \approx N \ln N - N$ . ]

- (c) Now consider that  $N_f$  such atoms are adsorbed as a mobile two-dimensional (2d) film on a solid surface of area  $\sigma$ . Obtain an expression for the Helmholtz free energy of the mobile film (ideal 2d gas),  $A_f$ , and use it to show that the chemical potential of the film,  $\mu_f$ , can be written

$$\mu_f - \mu_f(0) = -RT \ln \frac{\sigma}{\Lambda^2 N_f},$$

where  $\mu_f(0)$  is the chemical potential of the adsorbed atoms at 0 K. [8]

- (d) If equilibrium were established between the gas atoms free to move in a container of volume,  $V$ , and the mobile surface film of area  $\sigma$ , show that the fraction of the atoms adsorbed on the surface would be

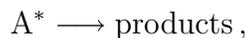
$$\frac{N_f}{N} = \frac{x}{1+x} \quad x = \frac{\sigma\Lambda}{V} e^{-\Delta E_0/RT},$$

where  $N = N_g + N_f$  is the total number of atoms, and  $\Delta E_0 = E_f(0) - E_g(0)$  is the molar zero-point energy difference between the adsorbed atoms and the gas atoms. Sketch the likely dependence of  $N_f$  and  $N_g$  on temperature. [8]

- (e) Discuss which features of the derivation involved in parts (c) and (d) would need to be modified if the adsorbed atoms formed an *immobile* surface film. (Detailed derivation of relevant equations is not required.) [4]

## 8. Chemical Reaction Rates and Reaction dynamics

The RRK theory of unimolecular reactions predicts the rate constant for the reaction step,



to have the following dependence on internal energy,  $E$ , above the threshold,  $E_0$ ,

$$k(E) = k^\ddagger \left( \frac{E - E_0}{E} \right)^{s-1} \quad \text{for } E \geq E_0$$

- What are the assumptions upon which the above RRK expression for  $k(E)$  is based? Define  $s$  and  $k^\ddagger$  appearing in the above equation. [5]
- Sketch the energy dependence of the predicted rate constant,  $k(E)$ , for  $s = 1$ , and for two higher values of  $s$ . Provide a physical explanation for the dependence of  $k(E)$  on energy,  $E$ , and  $s$ . [5]
- The unimolecular dissociation of the molecule NCNO to CN and NO has been studied as a function of time using a picosecond pump and probe (flash photolysis) method. The following dissociation rate constants (in  $\text{s}^{-1}$ ) were observed as a function of energy above the threshold,  $E_0 = 17080 \text{ cm}^{-1}$

$(E - E_0)/\text{cm}^{-1}$	50	200	300	500	700
$\ln \{k(E)\}$	22.1	23.9	24.4	24.9	25.3

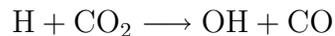
- Use a graphical procedure to calculate the RRK parameters  $k^\ddagger$  and  $s$ . Comment on the value of  $s$  you obtain. [8]
- Use your answer to part (c)i to estimate the limiting high pressure rate constant,  $k_\infty$ , for the *thermal* unimolecular dissociation of NCNO at 1000 K. [2]
- In reality the RRK theory estimate of  $k_\infty$  is likely to be poor, and in general the theory cannot account for the wide variation in the Arrhenius  $A_\infty$ -factors from one reaction to another.

What improvements could be made to the RRK model? How does the transition state theory expression for  $k_\infty$ ,

$$k_\infty = \frac{k_B T}{h} \frac{q^\ddagger}{q} e^{-E_0/k_B T},$$

help to rationalize the differences in  $A_\infty$ -factors referred to above? [4]

- (d) Pump and probe experiments have also been performed on the *bimolecular* reaction



in which reaction was initiated by laser photolysis of HI bound to  $\text{CO}_2$  in an  $\text{OCO} \cdots \text{HI}$  van der Waals complex. These measurements suggest that OH is generated on a timescale of about  $3 \times 10^{-12}$  s at a collision energy of  $E_t \sim 170 \text{ kJ mol}^{-1}$ .

- i. Use your knowledge of the typical vibrational frequency of CO modes in molecules to determine an order-of-magnitude estimate of a CO vibrational period. What does your estimate suggest about the  $\text{H} + \text{CO}_2$  reaction mechanism under the conditions described above? [5]
- ii. What further evidence about the reaction mechanism could be provided by a crossed-molecular beam study of the  $\text{H} + \text{CO}_2$  bimolecular reaction? [5]

9. *Quantum Mechanics*

- (a) Explain briefly why the *variational principle* is useful in quantum mechanics. [4]  
(b) Prove that for a trial wavefunction

$$\psi = \sum_n c_n \chi_n$$

the expectation value of the energy,

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle},$$

satisfies the equation

$$\langle E \rangle - E_0 \geq 0,$$

where  $E_0$  is the lowest possible eigenvalue of  $\hat{H}$  (i.e. the true ground state energy), and where the non-degenerate, orthonormal functions  $\chi_n$  satisfy the equation  $\hat{H}\chi_n = E_n\chi_n$ . [5]

- (c) Use the variational principle to show that the trial function  $\psi(r) = N e^{-\alpha r}$ , with  $r$  in atomic units and normalization constant  $N = (\alpha^3/\pi)^{1/2}$ , yields the following estimate for the ground state energy (also in atomic units) of a hydrogen-like atom of charge number  $Z$

$$\langle E \rangle = \frac{\alpha^2}{2} - \alpha Z.$$

Use this expression to find the best estimate of the ground state energy of the H atom. [10]

How does the value you obtain compare with the true ground state energy of the H atom? [2]

[Note that for a spherically symmetric wavefunction the Hamiltonian for the H atom may be written (in atomic units)

$$\hat{h} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} \quad \text{with} \quad \nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r,$$

and that

$$\int_0^\infty x^n e^{-sx} dx = \frac{n!}{s^{n+1}}. ]$$

(d) In atomic units the Hamiltonian for the He atom may be written

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}},$$

where  $\hat{h}_i$  is the hydrogenic Hamiltonian for electron  $i$ , as defined in part (c), but with  $r = r_i$ , and  $r_{12}$  is the electron-electron separation.

A simple trial spatial wavefunction  $\Psi$  for the ground state of the He atom (i.e. the state of  $1s^2$  configuration) can be written in terms of the normalized wavefunctions  $\psi(r_1)$  and  $\psi(r_2)$  of part (c) as

$$\Psi = \psi(r_1) \psi(r_2) \equiv |1\ 2\rangle. \quad (1)$$

Derive an expression for  $\langle E \rangle$  in terms of the parameter  $\alpha$ . [5]

$$\left[ \text{Note that } \langle 1\ 2 | \frac{1}{r_{12}} | 1\ 2 \rangle = \frac{5}{8} \alpha. \right]$$

(e) Using your result from part (d), determine the best estimate of the ground state energy of the He atom in atomic units. What does the value of  $\alpha$  you obtain suggest about the ground state wavefunction of He compared with that for the hydrogen atom? [5]

(f) Explain whether a trial wavefunction of a simple product form, such as that given in equation 1, could ever be an eigenfunction of the Hamiltonian for the He atom. [3]

10. *Photochemistry*

- (a) Three processes of absorption and emission of light are absorption, spontaneous emission and stimulated emission.
- Describe briefly what happens in each process at a molecular level. [3]
  - Indicate the factors determining the rate of each process in a two-level system. [4]
- [Equations for the Einstein coefficients are not expected.]
- Which process is dominant in fluorescence and which in laser action? [2]
- (b) Comment on THREE of the following statements, giving equations and/or examples where applicable:
- Beer's law is strictly valid only for light of a narrow range of wavelengths within which the absorption coefficient is constant. At high light intensities it may break down completely. In some circumstances "negative absorption" may occur, where the transmitted light is more intense than the incident light.
  - Kasha's rule, that emission occurs from the lowest state of each multiplicity, is valid for most luminescent substances. It breaks down for very small molecules in the gas phase and for some special polyatomic molecules such as azulene and its derivatives and thiocarbonyls in solution, which emit from  $S_2$ .
  - Fluorescence emission bands generally lie to the red of the corresponding absorption bands, and may relate to the shape of the absorption as mirror images. For some substances the magnitude of the red shift between absorption and emission varies over a wide range according to the nature of the solvent.
  - The products of a photochemical reaction are often chemically distinct from the products of a thermal reaction with the same reactant(s). The nature of the products may depend on the wavelength of the light used, or on the nature of the solvent. For instance, solvents containing heavy-atoms such as ethyl iodide or dibromoethane may favour different products from those produced in a hydrocarbon solvent.
  - Pyrene (and some other compounds) shows fluorescence of different colours in concentrated and dilute solution. In concentrated solution at low temperature light in the fluorescence wavelength band exhibits a two-component decay, with one short and one long lifetime.

[All parts will be given equal weight.] [25]

## 11. Atmospheric Chemistry

- (a) The mean temperature of the Earth's surface is higher than the mean temperature expected from the balance of absorbed and emitted radiation.
- Explain qualitatively why this is so. [5]
  - Identify the atmospheric constituents which make major contributions to surface warming. [4]
  - Discuss whether or not the contributions of different gases are additive, and how the warming effect may depend on their concentrations. [4]
- (b)
- Explain why the presence of methane in the troposphere is important for the oxidation of NO to NO<sub>2</sub> and thus for the formation of tropospheric ozone. [5]
  - The main reaction removing CH<sub>4</sub> is reaction with OH, for which the rate constant is  $7.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The mean concentration of OH in the troposphere is  $6 \times 10^5 \text{ molecules cm}^{-3}$ . Estimate the lifetime of CH<sub>4</sub> in the troposphere. [5]
- (c) The most intense feature in the Earth's dayglow is emission from the transition  $\text{O}_2(^1\Delta_g) \rightarrow \text{O}_2(^3\Sigma_g^-)$ .
- How is the excited molecular oxygen  $\text{O}_2(^1\Delta_g)$  formed? [3]
  - The  $v' = 0 \rightarrow v'' = 0$  vibrational band of this system is the most intense as observed from space, but very weak as seen from the ground, whereas the  $v' = 0 \rightarrow v'' = 1$  band can be observed equally well from outside or within the atmosphere. Suggest a reason. [3]
  - The infrared atmospheric band originates at altitudes around 50 km, where the gas density is  $2 \times 10^{16} \text{ molecules cm}^{-3}$ , from the transition  $\text{O}_2(^1\Delta_g) \rightarrow \text{O}_2(^3\Sigma_g^-)$  whose radiative lifetime is 44 min.  
  
In a total solar eclipse, the intensity of the band was found to drop with a half-life of 108 s. Obtain a rate constant for quenching of the excited state and comment on the result. [5]
- [Note. A typical quenching rate constant is  $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .]

## 12. *Molecular Interactions*

- (a) i. Explain what is meant by an *amphiphile*. [2]
- ii. Describe some of the properties of solutions of amphiphilic molecules that lead to the widespread use of amphiphiles (e.g., surfactants) in practical applications. [6]
- iii. What is meant by the *critical micelle concentration*? [2]
- iv. Discuss how factors such as entropy of mixing, the hydrophobic effect and head group repulsions influence the behaviour of amphiphilic molecules in aqueous solutions and explain how these factors can lead to the formation of micelles. [5]
- (b) The dimensionless ratio  $v/al$  is a useful predictor of the shape of aggregates of amphiphiles in aqueous solutions, where  $v$  and  $l$  are the volume and length, respectively, of the hydrophobic part of the amphiphile and  $a$  is the area of the hydrophilic head group at the surface of the aggregate.
- i. Use simple geometric arguments to show that the maximum value of  $v/al$  is  $1/3$  for spherical micelles,  $1/2$  for cylindrical micelles and  $1$  for planar bilayers. [7]
- ii. Suggest how the size and shape of small, spherical micelles of an ionic surfactant might be affected by addition of
- A. an electrolyte,  
B. a cosurfactant, such as decanol,  
C. a non-polar material. [6]
- iii. What are the differences between an *emulsion* and a *microemulsion*? One common form of microemulsion contains small ( $\sim 10$  nm diameter) spherical droplets of water in a continuous oil phase. Suggest what characteristics a surfactant would need to have to stabilize a ‘water-in-oil’ microemulsion. [6]

13. *Physical Chemistry of Elemental and Combined Hydrogen*

Explain SIX of following observations, making quantitative deductions where appropriate.

- (a) In the rotational Raman spectrum of  $\text{H}_2$ , the lines of each branch alternate in intensity with an intensity ratio approaching 3:1 at high temperature. In the equivalent spectrum of  $\text{D}_2$  there is intensity alternation approaching a ratio of 2:1, but there is no such alternation in the rotational Raman spectrum of HD.
- (b) Hydrogen atom removal is the rate-determining step in base-catalysed bromination of propanone. The rate of this reaction is about 7 times slower at 298 K if  $\text{C}_3\text{D}_6\text{O}$  is used instead of  $\text{C}_3\text{H}_6\text{O}$ . In some hydrogen atom abstraction reactions the Arrhenius plot for an H-compound deviates more from linearity than a similar plot for a D-compound.

[The C–H stretching frequency is  $8.4 \times 10^{13} \text{ s}^{-1}$ .]

- (c) If molecular hydrogen is cooled to 20 K in the presence of active charcoal or a paramagnetic salt, the gas that remains after removal of the catalyst has a different heat capacity compared with normal hydrogen over a wide temperature range. There is a maximum in its heat capacity as a function of temperature.
- (d) The rate constant for intersystem crossing from  $T_1$  to  $S_0$  in naphthalene is decreased by a factor of ten if all the hydrogen in the molecule is replaced by deuterium. The phosphorescence lifetime of naphthalene- $h_8$  in a rigid glass at 77 K is 2.3 s, but that of naphthalene- $d_8$  is 18.4 s.

[Hint: To obtain full credit you should calculate the rate constants from these data.]

- (e) Excited hydrogen atoms with  $n = 2$  are produced when  $\text{H}_2$  absorbs light of photon energy above 14.69 eV. (The excited H atoms can be detected by observing the light they emit at 121.57 nm.)  $\text{H}^+$  ions are produced at energies above 18.1 eV and  $\text{H}_2^+$  ions are produced above 15.45 eV.

[Hint: Deduce the dissociation energies  $D_0$  of  $\text{H}_2$  and  $\text{H}_2^+$ .]

- (f) The reaction



generates rotationally excited BaI, and the rotational population distribution for these products can be used to estimate the dependence of the reaction probability on impact parameter,  $P(b)$  (known as the opacity function).

- (g) Neutron scattering is much better than X-ray scattering for studying the structure of hydrated ions. Isotopic substitution of D for H has a major influence on neutron scattering but a negligible effect on the scattering of X-rays.
- (h) Signal strengths in deuterium NMR are much weaker than in proton NMR. In a fully deuterated organic molecule, the  $^2\text{H}$ -NMR spectrum generally contains many more lines than the  $^1\text{H}$ -NMR spectrum of the fully protonated analogue. The chemical shifts in the two molecules are the same, but the coupling constants in the perdeuterated molecule are much smaller.

[Each part will be given equal weight.]

[34]

If you use this answer sheet for question 4 **B**, put your candidate number in the box below and attach the sheet to your script.

CANDIDATE NUMBER:

QUESTION 4 Part **B**

