

DCHA 2705

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY I

Friday, 6th June 2003, 9.30 a.m. to 12.30 p.m.

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Answer *FIVE* out of nine questions

Please begin your answer to each question on a new page

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

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

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

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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	$\epsilon_0$	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Avogadro constant	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	$u$	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	$\mu_B$	$9.274 \times 10^{-24} \text{ J T}^{-1}$

### Other conventions

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

## 1. Vibrational Spectroscopy

The vibrational energies of a diatomic molecule are often approximated by the formula

$$E/hc = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x_e.$$

- (a) Discuss connections between the parameter  $\omega_e$ , the relevant atomic masses and the curvature of the potential energy function. [3]
- (b) How can the dissociation energy,  $D_e$ , of the potential function be estimated from a knowledge of  $\omega_e$  and  $\omega_e x_e$ ? [4]
- (c) The infra-red spectrum of  $\text{H}^{35}\text{Cl}$  contains a strong fundamental band at  $2885.31 \text{ cm}^{-1}$  and a weaker band at  $5664.98 \text{ cm}^{-1}$ . Determine  $\omega_e$  and  $\omega_e x_e$ . [5]
- (d) Predict  $\omega_e$  and  $\omega_e x_e$  for  $\text{D}^{35}\text{Cl}$ . [4]
- (e) With reference to the relevant transition moments, describe circumstances in which infra-red absorption transitions with  $\Delta v = 1$  are allowed, while those with  $\Delta v = 2$  are strictly forbidden. [4]

## 2. Thermodynamics

- (a) Use the fundamental equation  $dG = Vdp - SdT$  to show that the chemical potential of a perfect gas satisfies

$$\mu = \mu^\ominus + RT \ln \left( \frac{p}{p^\ominus} \right),$$

where  $p^\ominus$  is the standard pressure ( $p^\ominus = 1 \text{ bar} \simeq 1 \text{ atm}$ ). What is the analogous expression for the chemical potential of the  $J$ -th component in a mixture of perfect gases? [5]

- (b) By equating the chemical potentials of water in the liquid and vapour phases, show that the equilibrium vapour pressure of water in air at temperature  $T$  is given by

$$p_{\text{H}_2\text{O}} = p^\ominus \exp \left( -\Delta_{\text{vap}}G^\ominus / RT \right),$$

where  $\Delta_{\text{vap}}G^\ominus$  is the standard molar Gibbs free energy of vaporisation of water. What assumptions have you made about the liquid and vapour phases? [5]

- (c) By considering how  $\Delta_{\text{vap}}G^\ominus$  varies with temperature, i.e.,

$$\left( \frac{\partial[\Delta_{\text{vap}}G^\ominus / T]}{\partial T} \right)_p = -\frac{\Delta_{\text{vap}}H^\ominus}{T^2},$$

show that the result in (b) above leads (approximately) to

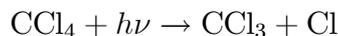
$$\ln \left( \frac{p_{\text{H}_2\text{O}}}{p^\ominus} \right) = \frac{\Delta_{\text{vap}}H^\ominus}{R} \left( \frac{1}{T_{\text{vap}}} - \frac{1}{T} \right),$$

where  $T_{\text{vap}}$  is the normal boiling point of liquid water. Again highlight any assumptions in your argument. [5]

- (d) One mole of liquid water and one mole of air are heated gently in a container sealed by a piston under a total pressure of one atmosphere. Calculate the vapour pressure of water in the container once all of the liquid water has evaporated, and hence, given that  $\Delta_{\text{vap}}H^\ominus$  of water is approximately  $44 \text{ kJ mol}^{-1}$  at temperatures approaching  $T_{\text{vap}} = 373 \text{ K}$ , estimate the temperature at which the evaporation is complete. Comment on your result. [5]

### 3. Gas Kinetics and Atmospheric Chemistry

- (a) Chlorine atoms are produced by the photolysis reaction

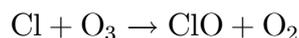


using a  $\mu\text{s}$  pulse of total energy 0.1 J, around a central wavelength  $\lambda = 180 \text{ nm}$ .

- (i) Estimate the number of photons in the pulse. [3]

- (ii) Assuming an absorption coefficient of  $\epsilon = 2 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ , use the Beer-Lambert law to estimate the concentration,  $c'$ , of Cl atoms produced when the flash illuminates the side of a reaction cell with area  $100 \text{ cm}^2$  and length  $10 \text{ cm}$  containing  $\text{CCl}_4$  at a concentration  $c = 2 \times 10^{15} \text{ molecules cm}^{-3}$ . [6]

- (b) The kinetics of the elementary reaction

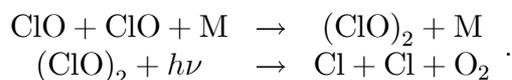


were studied in the above apparatus at 260 K by following the decay of the Cl atom absorption intensity at an initial ozone concentration of  $1.4 \times 10^{14} \text{ molecules cm}^{-3}$ . Assuming that the absorption intensity,  $I_{\text{abs}}$ , can be taken to be proportional to the Cl atom concentration, use the data below to determine the rate constant for the reaction.

[7]

$t/\text{ms}$	$I_{\text{abs}}(t)/I_{\text{abs}}(t=0)$
0.25	0.595
0.5	0.353
0.75	0.210

- (c) ClO radicals are known to form weakly bound dimers, which photolyze to produce Cl atoms, by the reactions

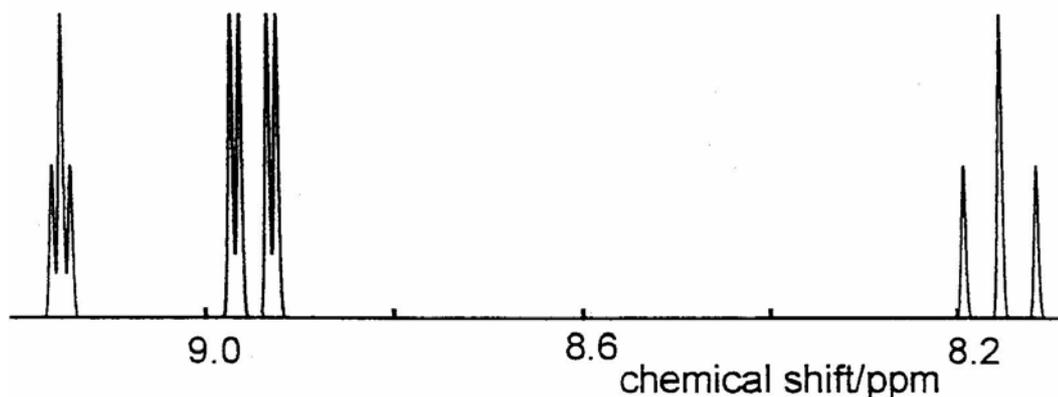


Comment on the relevance of these processes to the appearance of an ozone hole above the Antarctic in the spring. [4]

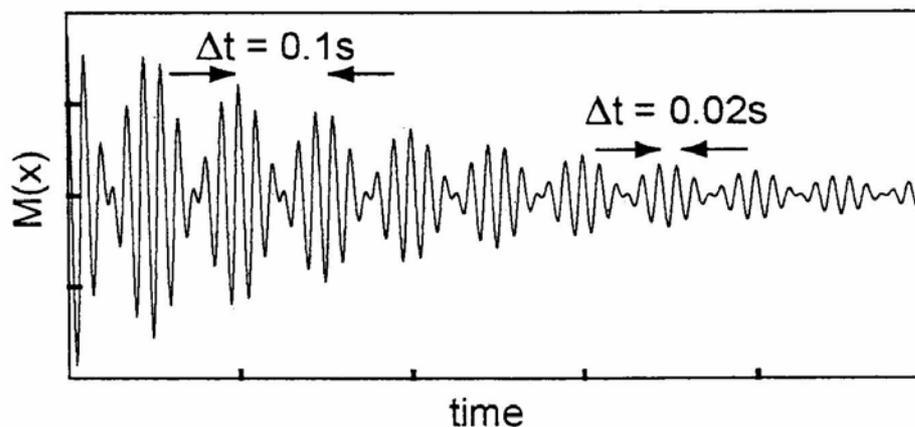
#### 4. Nuclear Magnetic Resonance

Answer **three** parts. All parts carry equal marks.

- (a) Account for the  $^1\text{H}$  NMR spectrum of an isomer of dinitrobenzene shown below.



- (b) Explain what is meant by dipolar coupling. How does this affect the spin lattice relaxation time in NMR? Suggest reasons why  $T_1$  for the central  $^{13}\text{C}$  in tetramethyl methane is very much longer than that for the outer carbon atoms.
- (c) Explain the basis of free induction decay in NMR. The free induction decay of a system containing a symmetrical doublet has the appearance shown below. Deduce the appearance of the corresponding NMR spectrum.



- (d) The NMR spectrum of dimethyl nitrosamine,  $(\text{CH}_3)_2\text{N}-\text{NO}$ , at 440 K, when the rate constant for internal rotation is  $9.9 \text{ s}^{-1}$ , consists of two lines separated by  $50 \text{ s}^{-1}$ . Assuming an activation energy of  $110 \text{ kJ mol}^{-1}$ , predict the appearance of the spectrum at 510 K. How does the appearance of the spectrum evolve at temperatures between 440 and 510 K?

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## 5. Molecular Interactions: Polymers

- (a) What is the radius of gyration of a polymer and how does it vary with molecular weight in a  $\theta$  solvent? [3]
- (b) The following values of the radius of gyration,  $R_g$ , of three different molecular weight samples of poly(styrene) were obtained in cyclohexane at 35°C (a  $\theta$  solvent) and in CS<sub>2</sub> (a good solvent) at room temperature:

$M_n/\text{g mol}^{-1}$	80000	200000	750000
$R_g$ in cyclohexane/nm	7.8	12.3	23.8
$R_g$ in CS <sub>2</sub> /nm	9.6	16.6	36.7

- (i) Determine from the data how the radius of gyration varies with molecular weight in each case. (You may find it helpful to use a log-log plot.) [4]
- (ii) Suggest reasons why the variation might be different for the two solvents. [3]
- (iii) Calculate what the root mean square end-to-end distance  $R_0$  would be for poly(styrene) of  $M_n = 200000 \text{ g mol}^{-1}$  in a  $\theta$  solvent if every chemical monomer unit behaved like a random flight segment. (A monomer unit of poly(styrene) has a molecular weight of 104 g mol<sup>-1</sup> and a length of 0.26 nm.) [3]
- (iv) By comparing the value of  $R_0$  calculated in (iii) with the value of  $R_0$  calculated from  $R_g$  in the table, calculate the number of chemical monomer units that make up a random flight segment in poly(styrene) ( $R_0 = R_g \times \sqrt{6}$ ). [3]
- (c) The radius of gyration of a sample of poly(ethylene oxide) (PEO) of molecular weight  $M_n = 200000 \text{ g mol}^{-1}$  in a  $\theta$  solvent was found to be 14.5 nm. Taking a chemical monomer unit to have a molecular weight of 44 g mol<sup>-1</sup> and a length of 0.36 nm, calculate the number of chemical monomer units that make up a random flight segment in PEO. Why is this different from the value for poly(styrene)? [4]

## 6. Statistical Mechanics

The torsional motion of the methyl group in solid nitromethane at low temperatures can be approximated by a two-level quantum system with degeneracies  $g_0 = g_1 = 4$  and an energy level spacing of  $\Delta\varepsilon = \varepsilon_1 - \varepsilon_0 \simeq 0.5 \text{ cm}^{-1}$ .

(a) Write down an expression for the molecular partition function of this two-level system. [2]

(b) Obtain an expression for the molar internal energy  $E_m(T)$  of the system and sketch the behaviour of  $E_m(T)$  as a function of  $T$ . [6]

(c) Show that the heat capacity of the system is given by

$$C_{V,m}(T) = N_A k_B \left( \frac{\Delta\varepsilon}{k_B T} \right)^2 \frac{e^{-\Delta\varepsilon/k_B T}}{(1 + e^{-\Delta\varepsilon/k_B T})^2}.$$

Discuss the behaviour of  $C_{V,m}(T)$  in the limits (i)  $k_B T/\Delta\varepsilon \ll 1$  and (ii)  $k_B T/\Delta\varepsilon \gg 1$ . [6]

(d) Without doing a detailed calculation, write down what you would expect to find for the molar entropy of the system,  $S_m(T)$ , in each of the two limiting regimes specified in part (c). [4]

(e) Speculate briefly on why a paramagnetic catalyst, such as  $\text{O}_2$ , is needed to achieve thermal equilibrium between the two levels. [2]

## 7. Quantum Mechanics

The spherically symmetric (“s-orbital”) wavefunctions of a particle of mass  $m$  in a sphere of radius  $a$  satisfy a Schrödinger equation of the form

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} [r\psi_n(r)] + V(r)\psi_n(r) = E_n\psi_n(r),$$

where the potential energy operator  $V(r)$  is given by

$$V(r) = \begin{cases} 0, & 0 \leq r < a \\ \infty & r > a. \end{cases}$$

- (a) Letting  $\psi_n(r) = \phi_n(r)/r$ , show that  $\phi_n(r)$  satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} \phi_n(r) = E_n \phi_n(r)$$

in the region  $0 \leq r < a$ , and explain why this reduced wavefunction must satisfy the boundary conditions  $\phi_n(0) = 0$  and  $\phi_n(a) = 0$ . [5]

- (b) Hence show that the solutions  $\psi_n(r)$  of the original Schrödinger equation are given to within a normalization constant  $N_n$  by

$$\psi_n(r) = \begin{cases} \frac{N_n}{r} \sin\left(\frac{n\pi r}{a}\right), & 0 \leq r < a \\ 0, & r > a. \end{cases} \quad [5]$$

- (c) Find the value of the normalization constant  $N_n$  such that

$$\int_0^\infty \psi_n(r)^2 4\pi r^2 dr = 1. \quad [5]$$

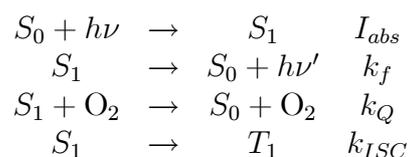
[Hint:  $2 \sin^2 x = 1 - \cos 2x$ .]

- (d) It is believed from electron spin resonance measurements that when  $\text{N}(^4S)$  atoms are trapped inside  $\text{C}_{60}$  they move around freely within the central cavity. Given that this motion can be modelled by that of a point particle in a sphere with an effective radius of 30 pm, calculate the most probable distance of the nitrogen nucleus from the centre of the cage in the low temperature limit where only the ground state of the cavity motion is populated. [5]

## 8. Photochemistry

(a) Explain why the fluorescence emission spectrum of a polyaromatic molecule in solution often mirrors the shape of the absorption spectrum, regardless of the excitation frequency. [5]

(b) The fluorescence dynamics of perylene ( $C_{20}H_{12}$ ) in benzene ( $C_6H_6$ ) are modelled in the presence of dissolved oxygen by the kinetic scheme



Give an expression for the fluorescence quantum yield,  $\phi_f$ , under conditions of steady illumination at frequency  $\nu$ . Use the data in the following table to determine the ratios  $k_Q/k_f$  and  $k_{ISC}/k_f$ . [8]

$[O_2]/10^{-3}\text{mol dm}^{-3}$	$\phi_f$
0.5	0.824
1.0	0.768
1.5	0.719

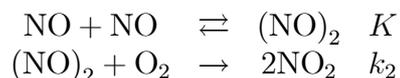
(c) Obtain an expression for the decay of fluorescence intensity following a short excitation pulse in the absence of oxygen. Hence use the fluorescence intensity data below to determine the rate coefficients  $k_Q$ ,  $k_f$  and  $k_{ISC}$ . [7]

$t/\text{ns}$	$I_f(t)/I_f(t=0)$
1.0	0.819
3.0	0.549
5.0	0.368

## 9. Properties of Nitric Oxide

Comment on the following properties of nitric oxide.

- (a) The reaction of NO with O<sub>2</sub> obeys the following mechanism,



and has a rate constant that decreases with increasing temperature. [5]

- (b) The infrared spectrum of NO vapour at 200 K shows an intense band with P, Q and R branches centred at 1846 cm<sup>-1</sup>, and additional less intense bands at lower frequencies, whose intensity increases with decreasing temperature. [5]

- (c) The residual (spectroscopic minus calorimetric) entropy of NO is

$$S_{\text{spec}} - S_{\text{cal}} = \frac{1}{2}R \ln 2. \quad [4]$$

- (d) At 144 K, the second virial coefficient,  $B$ , of nitric oxide vapour is  $-0.124 \text{ dm}^3\text{mol}^{-1}$ , whereas that of N<sub>2</sub> is  $-0.082 \text{ dm}^3\text{mol}^{-1}$ . [3]

- (e) The molar entropy of vaporization of NO at its boiling point of 121 K is  $113.5 \text{ J K}^{-1}\text{mol}^{-1}$ , whereas that of N<sub>2</sub> at its boiling point of 77 K is  $72.0 \text{ J K}^{-1}\text{mol}^{-1}$ . [3]