

DCHA 2713

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Tuesday, 4th June 2002, 2.20 p.m. to 5.30 p.m.

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Candidates should 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 on page 2 of this paper.

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1. Valence/molecular electronic spectroscopy
2. Reaction rates
3. Thermodynamics
4. Molecular interactions
5. Interfacial kinetics and surfaces
6. Molecular spectroscopy/group theory
7. Quantum mechanics
8. Liquid kinetics
9. Statistical mechanics
10. Atomic spectroscopy
11. Nuclear magnetic resonance
12. Photochemistry/reaction dynamics
13. Polymers

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

### 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
1 Da	=	1 g mol <sup>-1</sup>	1 L = 1 dm <sup>3</sup> 1 M = 1 mol L <sup>-1</sup>

## 1. Valence/Molecular Electronic Spectroscopy

(a) Explain briefly what is meant by the Born-Oppenheimer approximation, and the notion of a potential energy function. [6]

Discuss, and explain the physical basis of, the Franck-Condon principle. Include in your answer an explanation of the following terms: vertical transition, transition dipole moment, Franck-Condon overlap factor. Illustrate your discussion with a diagram showing potential energy curves, associated vibrational energy levels, and the vertical transition. [10]

What physical factors influence the spacing between vibrational levels? [2]

(b) The most intense transition between the ground state of a certain diatomic molecule and a particular excited electronic state, is to the  $v' = 4$  vibrational level of the upper state. The following data give the spectral lines ( $\tilde{\nu}$ , in  $\text{cm}^{-1}$ ) associated with transitions to the  $v' = 4 - 9$  levels of the upper electronic state:

$v'$ :	4	5	6	7	8	9
$\tilde{\nu}(\text{cm}^{-1})$ :	63,120	64,799	66,424	67,995	69,512	70,975

(i) Using a suitable linear extrapolation, estimate the number of vibrational levels in the excited electronic state, and the dissociation energy ( $D_0$ ) of that state. [8]

(ii) Assuming that molecular rotations are described adequately by the rigid rotor model, show that the R-branch lines associated with transitions to a given vibrational level of the upper electronic state may be expressed in the form

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2.$$

$B'$  and  $B''$  denote respectively the rotational constants associated with the appropriate vibrational levels of the excited and ground electronic states. [4]

(iii) Sketch the appearance of the R-branch, and explain what is meant by a *band head*. [2]

If a band head appears in the R-branch, what may be inferred about the relative bond lengths of the ground and excited electronic states? [2]

## 2. Reaction Rates

Answer all parts.

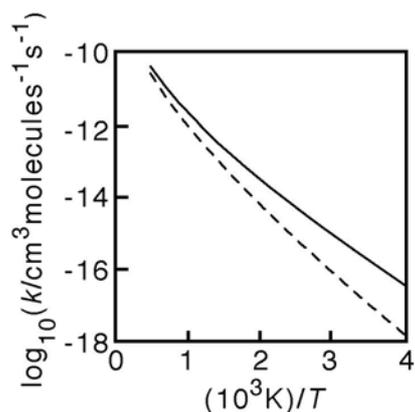
Note that detailed numerical calculation of rate coefficients is *not* required for any part of this question.

Where appropriate you may use without proof the transition state theory expression (written for an A + BC reaction)

$$k(T) = \frac{k_B T}{h} \frac{q^\ddagger}{q_A q_{BC}} e^{-\Delta E_0/RT}$$

where the  $q$  terms are molecular partition functions per unit volume.

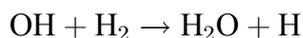
(a) The figure below shows the Arrhenius plot of the rate constants for the reactions

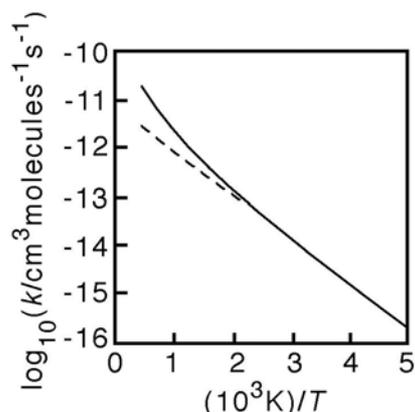


Use transition state theory arguments to explain qualitatively why the rate constants for the two reactions differ.

What other factors beyond those accounted for in transition state theory may need to be considered to obtain a quantitative estimate of the kinetic isotope effect for these reactions? Why does the Arrhenius plot for the  $\text{D} + \text{H}_2$  reaction look more curved at low temperature than that for the  $\text{H} + \text{D}_2$  reaction? [9]

(b) The following figure shows the Arrhenius plot of the rate constant of the reaction



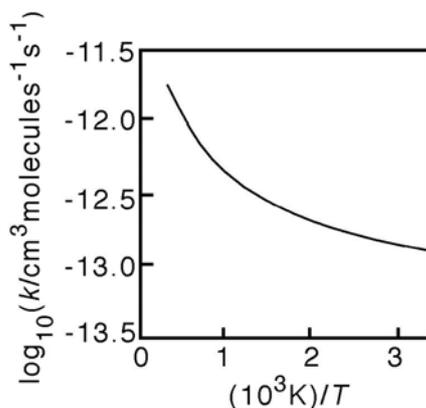
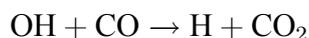


(The dashed line is a straight-line extrapolation of the low-temperature data).

The room temperature rate constant increases by a factor of over 100 upon excitation of  $H_2$  from  $v = 0$  to  $v = 1$ , but does not change significantly if OH is vibrationally excited.

Explain why vibrational excitation of  $H_2$  has such a dramatic effect on the room temperature rate constant, and suggest why this might have an important bearing on the non-Arrhenius behaviour of the thermal rate constant observed at high temperature. [9]

(c) The following figure shows the Arrhenius plot of the rate constant for the reaction



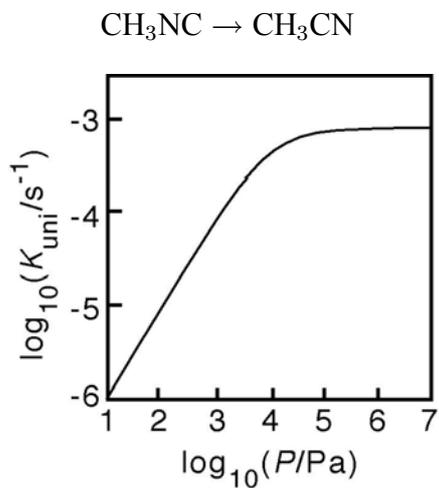
At temperatures below 300 K (not shown) the reaction rate constant and the products formed show significant pressure dependence.

How might the curvature in the Arrhenius plot for this reaction be explained using transition state theory? What does the pressure dependence suggest about the reaction mechanism at temperatures below 300 K? [8]

**Question continues**  
**Turn over**

2713 DCHA

(d) The following figure shows the pressure dependence of the rate constant for the isomerisation reaction at 500 K:



How could these data be used to test the Lindemann theory of unimolecular reactions? What modifications could be made to the Lindemann mechanism to improve the agreement with the experimental pressure dependence? [8]

### 3. Thermodynamics

The thermodynamic coefficient  $\mu_{JT} = (\partial T / \partial P)_H$  gives the change in temperature per unit pressure change, when a gas expands adiabatically such that the enthalpy ( $H$ ) is constant (a so-called Joule-Thomson expansion).

(a) Show that  $\mu_{JT}$  may be expressed as

$$C_p \mu_{JT} = - \left( \frac{\partial H}{\partial P} \right)_T$$

where  $C_p$  is the constant pressure heat capacity. Note that  $\left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1$ . [4]

(b) By considering  $dH$ , show that

$$\left( \frac{\partial H}{\partial P} \right)_T = V + T \left( \frac{\partial S}{\partial P} \right)_T.$$

Hence, using an appropriate Maxwell relation, show that

$$C_p \mu_{JT} = T \left( \frac{\partial V}{\partial T} \right)_P - V$$

and determine  $\mu_{JT}$  for a perfect gas. [6]

At sufficiently low pressures the equation of state of a real gas is given by

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m}$$

where  $V_m$  denotes the molar volume. The second virial coefficient  $B(T) = b - a/RT$  where  $a$  and  $b$  are positive constants.

(c) Show that  $\mu_{JT}$  for the gas may be expressed as

$$C_{p,m} \mu_{JT} = \frac{-b + \frac{2a}{RT}}{\left[ 1 + \frac{4P}{RT} \left( b - \frac{a}{RT} \right) \right]^{\frac{1}{2}}} \quad (1)$$

where  $C_{p,m}$  is the molar heat capacity.

You may find it helpful to note that  $\left[ 1 + \frac{4P}{RT} B(T) \right] = \left[ 1 + \frac{2B(T)}{V_m} \right]^2$ . [9]

(d)  $\mu_{JT}$  changes sign at the inversion temperature,  $T_1$ . Obtain an expression for  $T_1$ , and calculate it for the case of  $\text{CO}_2$  ( for which  $a = 0.52 \text{ Jm}^3\text{mol}^{-2}$  and  $b = 8.42 \times 10^{-5} \text{ m}^3\text{mol}^{-1}$ ). [4]

For  $T > T_1$ , does the gas cool down under a Joule-Thomson expansion, or does it heat up? Explain your reasoning. [2]

(e) For  $\text{CO}_2$  it is found experimentally that  $T_B/T_1 \simeq 0.48$ , where  $T_B$  is the Boyle temperature. Comment. [4]

(f) By considering equation (1) above, and neglecting any pressure dependence of  $C_{p,m}$ , explain why  $\mu_{JT}$  initially decreases as the pressure  $P$  is increased from zero for a fixed temperature in the interval  $T_B < T < T_1$ . What is the corresponding behaviour of  $\mu_{JT}$  for  $T > T_1$ ? [5]

#### 4. Molecular interactions

(a) Define the chemical potentials,  $\mu_A$  and  $\mu_B$ , of the species A and B in a two-component mixture.

[2]

(b) The non-ideal part of the chemical potentials can be expressed as a power series in the mole fractions,  $x_A$  and  $x_B$

$$\begin{aligned}\mu_A &= \mu_A^* + RT \ln x_A + \alpha_A x_B + \beta_A x_B^2 + \dots \\ \mu_B &= \mu_B^* + RT \ln x_B + \alpha_B x_A + \beta_B x_A^2 + \dots\end{aligned}$$

The Gibbs-Duhem equation at constant T and P can be written as

$$x_A d\mu_A + x_B d\mu_B = 0$$

By considering the change in  $\mu_A$  and  $\mu_B$ , in response to a change in composition  $dx_A (= -dx_B)$ , show that

$$\begin{aligned}\alpha_A &= \alpha_B = 0 \\ \beta_A &= \beta_B\end{aligned}$$

[8]

(c) Outline the principles of the regular solution model for mixtures of non-electrolytes.

The free energy of a regular solution is

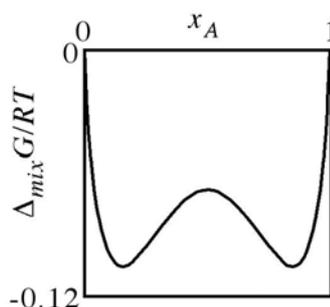
$$G = n[x_A \mu_A^* + x_B \mu_B^* + RT(x_A \ln x_A + x_B \ln x_B) + \beta x_A x_B]$$

where  $n = n_A + n_B$  is the total number of moles in the system. From the definition of chemical potential in (a), show that

$$\mu_A = \mu_A^* + RT \ln x_A + \beta x_B^2$$

[10]

(d) The figure below shows the free energy of mixing of a regular solution,  $\Delta_{mix}G$ , as a function of  $x_A$  for  $\beta/RT=2.5$ .



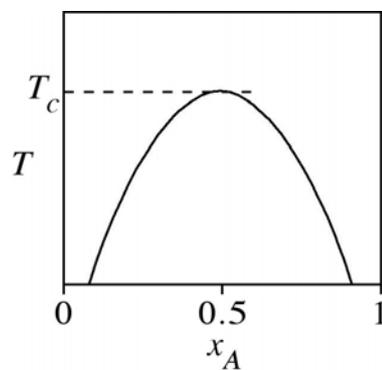
Use this diagram to explain why a two-component mixture can phase separate even though  $\Delta_{mix}G$  is everywhere negative.

[6]

2713 DCHA

Question continues

- (e) The figure below shows the phase diagram for a liquid-liquid mixture in the regular solution model.



By considering the sign of  $d^2\Delta_{mix}G/dx_A^2$  at  $x_A = \frac{1}{2}$ , show that the upper critical solution temperature,  $T_c$ , is given by

$$T_c = \beta/2R$$

[8]

## 5. Interfacial kinetics and surfaces

Answer BOTH Parts.

### Part A

The Butler-Volmer equation for the Faradaic current,  $i$ , at an electrode surface can be written

$$i = i_0 \left( \frac{[R]_0}{[R]_{bulk}} e^{(1-\alpha)F\eta/RT} - \frac{[O]_0}{[O]_{bulk}} e^{-\alpha F\eta/RT} \right)$$

where  $[R]$  and  $[O]$  are the concentrations of reduced and oxidised species, the subscripts '0' and 'bulk' refer to the surface and bulk concentrations and  $F$  is Faraday's constant.

(a) Define the overpotential,  $\eta$ , and explain the physical significance of the parameters  $i_0$  and  $\alpha$ . [4]

(b) The current,  $i$ , calculated from the Butler-Volmer equation is tabulated below for the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  at 298 K as a function of overpotential for initial concentrations of  $[\text{Eu}^{3+}] = [\text{Eu}^{2+}] = 0.01 \text{ M}$ .

$\eta/\text{mV}$	-20	-40	-60	-80	-100	-120
$i/\text{Am}^{-2}$	-2.8	-5.5	-9.8	-15.9	-25.0	-38.7

Construct a Tafel plot (i.e. a plot of  $\ln |i|$  against  $\eta$ ) and determine the values of  $i_0$  and  $\alpha$ , on the assumption that the surface and bulk concentrations are equal. [7]

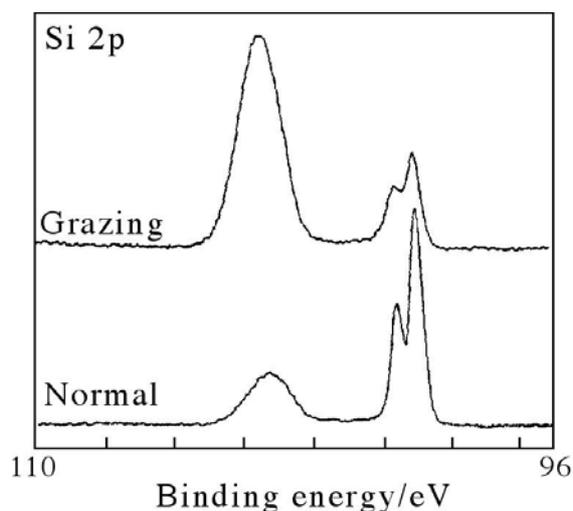
(c) (i) At sufficiently high overpotentials,  $[O]_0$  drops below  $[O]_{bulk}$  because diffusion cannot replenish  $O$  as fast as it is reduced at the electrode surface. A well-stirred solution can be treated as though  $[O]=[O]_{bulk}$  up to a distance,  $\delta$ , from the surface and then decreases linearly to a value of  $[O]_0$  at the surface. By considering the maximum flux of  $\text{Eu}^{3+}$  ions through this 'diffusion layer', calculate the limiting current at high overpotentials, assuming  $\delta = 25 \mu\text{m}$  and the diffusion coefficient,  $D$ , of  $\text{Eu}^{3+}$  ions is  $5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ . [4]  
(Fick's 1st Law:  $J = -D dc/dx$ ).

(ii) Hence sketch the Tafel plot for the  $\text{Eu}^{3+}/\text{Eu}^{2+}$  couple when mass transport limitations are taken into account. [2]

**Part B**

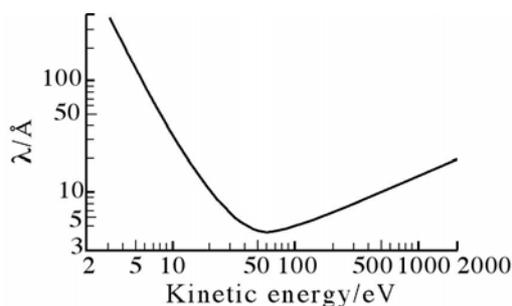
(a) Describe the physical processes leading to the emission of X-ray photoelectrons and Auger electrons from surfaces. How does surface sensitivity in X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy arise? [5]

(b) The figure below shows XPS spectra in the Si(2p) region obtained from a silicon wafer with a thin layer of SiO<sub>2</sub> on the surface, using Al K $\alpha$  X-rays at 1487 eV. The lower spectrum was obtained from electrons emitted along the surface normal ( $\theta = 0^\circ$ ) and the upper spectrum from electrons emitted at a grazing angle to the surface ( $\theta = 70^\circ$ )



Account qualitatively for the features in these spectra. [7]

(c) The probability of a photoelectron escaping from the surface without losing energy is given by  $\exp(-d/\lambda \cos \theta)$  where  $\lambda$  is the inelastic mean free path and  $d$  is the depth below the surface at which the photoelectron is emitted.  $\lambda$  for the Si(2p) photoelectrons may be estimated from the ‘universal curve’ of  $\lambda$  against kinetic energy shown below.



Assuming that the spectra in (b) have been normalised to the signal obtained from a bare silicon substrate at each angle, estimate the thickness of the SiO<sub>2</sub> layer. [5]

## 6. Molecular Spectroscopy/Group Theory

(a) Draw a diagram of ammonia, and identify on it the symmetry elements of the molecule. Hence determine the point group of ammonia. [4]

(b) How many vibrational modes does ammonia possess? Explain your reasoning.

Using the group tables provided, determine the *reducible* representation spanned by the coordinates of the four atoms of ammonia. Explain why, in this representation, the character for rotation about the  $z$ -axis in ammonia is zero.

What *irreducible* representations are spanned by centre-of-mass translation, and rotations about the centre-of-mass? Hence show that the vibrations in ammonia transform as  $2a_1+2e$ . [10]

(c) What is the *gross* selection rule for IR spectroscopy? Explain the origin of this selection rule.

State whether the vibrations identified in (b) are expected to be IR and/or Raman active.

The two non-degenerate modes of ammonia have vibrational wavenumbers centred at  $\tilde{\nu}_1 = 3337 \text{ cm}^{-1}$  and  $\tilde{\nu}_2 = 950 \text{ cm}^{-1}$ .

Based on the result given in (b), together with your knowledge of typical vibrational frequencies, sketch the two modes. Provide a physical rationale for either the IR or the Raman activity of the two modes. [8]

(d) Vibrational energy levels involving the  $\nu_2$  mode show a doublet structure, with doublet splittings which increase with number of quanta. Microwave spectroscopy suggests that the splitting is about  $0.8 \text{ cm}^{-1}$  in the  $\nu_2 = 0$  level.

Identify the origin of the splitting, explain its energy level dependence, and estimate the timescale of the process responsible for the splitting. [5]

(e) The classical rotational energy of a non-linear molecule can be written as

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

where  $J_\alpha$  is the angular momentum about axis  $\alpha$  with moment of inertia  $I_\alpha$ .

Use the correspondence principle to show that the quantum mechanical energy levels of an oblate top, for which  $I_a = I_b < I_c$ , can be written

$$E(J, K)/\text{cm}^{-1} = BJ(J+1) + (C-B)K^2$$

with  $B = h/8\pi^2cI_b$  and  $C = h/8\pi^2cI_c$ .

What is the significance of the  $K$  quantum number? Describe the rotational motion of an oblate top molecule, such as ammonia, in a rotational level with  $K = J$ . [7]

2713 DCHA

## 7. Quantum Mechanics

(a) Write down the Hamiltonian,  $\hat{H}_0(x)$ , for a simple harmonic oscillator of mass  $m$  and force constant  $k$ . Give the result for the corresponding energy levels, in terms of the oscillator frequency  $\omega_0 = [k/m]^{1/2}$ . [4]

What is the minimum energy the oscillator may possess, and why is it non-zero? [4]

The Hamiltonian for a pair of identical coupled oscillators may be expressed as

$$\hat{H} = \hat{H}_0(x_1) + \hat{H}_0(x_2) + \lambda \hat{V}$$

where the perturbation  $\hat{V} = kx_1x_2$ , and  $\lambda$  is a constant ( $0 \leq \lambda < 1$ ). For a single oscillator, the only non-zero matrix elements of  $x_i$  are  $\langle v_i + 1 | x_i | v_i \rangle = (\hbar/2m\omega_0)^{1/2} [v_i + 1]^{1/2}$ .

(b) Within second-order perturbation theory, the ground state energy of the system is given approximately by

$$E = E_0 + E'$$

where:

$$E' = -\lambda^2 \sum_{n(\neq 0)} \frac{|\langle n | \hat{V} | 0 \rangle|^2}{E_n - E_0}$$

Here  $|0\rangle$  and  $|n\rangle$  denote respectively the ground state and excited states for  $\lambda = 0$ , with corresponding energies  $E_0$  and  $E_n$ . The states  $|0\rangle$  and  $|n\rangle$  may be expressed in product form  $|v_1 v_2\rangle = |v_1\rangle \times |v_2\rangle$ , with  $|v_i\rangle$  referring to a single harmonic oscillator.

Show that within perturbation theory,

$$E = \hbar\omega_0 \left[ 1 - \frac{\lambda^2}{8} \right]. \quad [8]$$

(c) By transforming the coordinates from  $x_1$  and  $x_2$  to  $y_+ = \frac{1}{2}(x_1 + x_2)$  and  $y_- = \frac{1}{2}(x_1 - x_2)$ , show first that  $\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} = \frac{1}{2} \left( \frac{\partial^2}{\partial y_+^2} + \frac{\partial^2}{\partial y_-^2} \right)$ . Using this, show that  $\hat{H}$  becomes separable:

$$\hat{H} = \hat{H}_+(y_+) + \hat{H}_-(y_-) \text{ where } \hat{H}_+ \text{ and } \hat{H}_- \text{ each has harmonic oscillator form.} \quad [10]$$

Hence obtain an exact expression for the eigenvalues of  $\hat{H}$ . [4]

Show that to leading order in  $\lambda^2$ , the ground state energy  $E$  reduces to the result obtained from second-order perturbation theory. [4]

For small  $x$ ,  $[1 + x]^{1/2} \simeq 1 + \frac{1}{2}x - \frac{1}{8}x^2$ .

## 8. Liquid kinetics

Answer **Part A** and **Part B**.

### Part A

(a) The Born Equation provides an expression for the self-energy of an ion of charge  $ze$  and radius  $a$  in a dielectric medium of relative permittivity  $\epsilon_r$ :

$$G = \frac{N_A z^2 e^2}{8\pi\epsilon_r\epsilon_0 a} = \frac{69z^2}{\epsilon_r a} \text{ kJmol}^{-1}$$

if  $a$  is in units of nm. The Born Equation provides a means of estimating the effect of the dielectric constant of the solvent on the rates of activation-controlled reactions involving ions in solution.

Chloride ions react with methyl iodide by an  $S_N2$  mechanism:  $\text{Cl}^- + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{Cl} + \text{I}^-$ . The ionic radius of  $\text{Cl}^-$  is 0.18 nm and the radius of the transition state is  $\sim 0.4$  nm.

- (i) By considering the difference in the self-energies of the reactants and the transition state, estimate the ratio of rate constants for the above reaction in dimethyl formamide (DMF,  $\epsilon_r = 37$ ) and water ( $\epsilon_r = 80$ ) at 298 K. [5]
- (ii) The measured rate constant in DMF is more than  $10^5$  times faster than in water. Comment in the light of the prediction of the Born model. [2]

(b) The effect of ionic strength on the rates of reactions between ionic species (the kinetic salt effect) may be treated by Debye-Hückel theory. A calculation of the self-energy of an ion in the presence of the mean field of the other ions in solution gives the following expression for the activity coefficient of a species of charge  $z$  in a solution of ionic strength  $I$ .

$$\log \gamma = -Az^2\sqrt{I}$$

where  $A = 0.51$  for aqueous solutions at 298 K.

- (i) Show that for a bimolecular reaction between ions of charge  $z_A$  and  $z_B$ ,

$$\log(k/k_0) = 2Az_A z_B \sqrt{I}$$

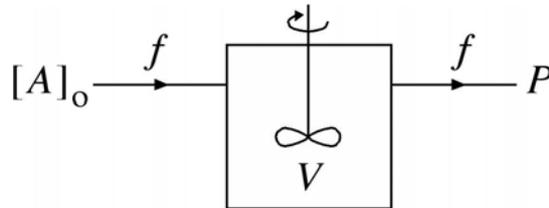
where  $k$  is the rate constant at ionic strength,  $I$ , and  $k_0$  is the rate constant at zero ionic strength. [5]

- (ii) Hence predict the value of  $k/k_0$  for the alkaline hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  at an ionic strength of 0.01 and at a temperature of 298 K. Compare with the experimental value of  $k/k_0 = 0.631$ . [2]

(c) Suggest reasons why a simple electrostatic model works so well in (b), given that it fails completely to predict the relative rates in (a). (You may wish to note that the Debye length in an aqueous solution with  $I = 0.01$  is 3 nm). [3]

**Part B**

Consider a simple reaction  $A \rightarrow P$  showing first-order kinetics:  $d[P]/dt=k[A]$ . The reaction is carried out in a large reaction vessel of volume  $V$ . The reagent  $A$  with concentration  $[A]_0$  enters the vessel with a flow rate  $f$ , and the product  $P$ , together with unreacted  $A$ , leaves with the same flow rate. The vessel is stirred vigorously so that the concentrations of reactants and products may be considered to be uniform throughout the vessel.



(a) Show that the steady-state concentration of  $A$  in the vessel is given by

$$\frac{[A]}{[A]_0} = \frac{1}{1 + k\tau}$$

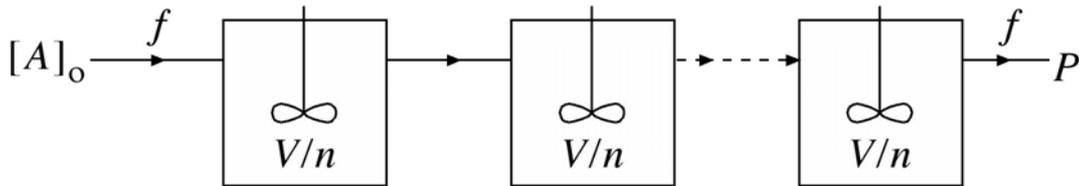
where the residence time,  $\tau = V/f$ .

Hence show that the extent of conversion,  $[P]/[A]_0$  is given by

$$\frac{[P]}{[A]_0} = \frac{k\tau}{1 + k\tau}$$

[6]

(b) Rather than having one large reactor of volume,  $V$ , a series of  $n$  smaller reactors of volume  $V/n$  can be connected in series, as shown schematically below.



Show that the extent of conversion is now

$$\frac{[P]}{[A]_0} = 1 - \frac{1}{(1 + k\tau_n)^n}$$

where  $\tau_n = V/nf$  is the residence time in each small reactor.

[4]

(c) For a particular industrial process, a conversion efficiency of at least 95% is required. Assuming that the rate constant,  $k = 0.01 \text{ s}^{-1}$ , calculate the maximum flow,  $f$ , that is consistent with the desired purity for

- (i) a single reactor of volume  $V = 1000 \text{ dm}^3$
- (ii) a three-stage reactor, each of volume  $V/3$ .

Comment on the result you obtain.

[7]

2713 DCHA

Turn over

## 9. Statistical Mechanics

In terms of the canonical partition function  $Q \equiv Q(N, V, T)$ , the internal energy and Helmholtz free energy are given respectively by  $U = k_B T^2 (\partial \ln Q / \partial T)_{N, V}$  and  $A = -k_B T \ln Q$ .

- (a) For a gas of independent particles, show that the entropy  $S$  is given in terms of the molecular partition function  $q$  by

$$\frac{S}{Nk_B} = \ln \left( \frac{qe}{N} \right) + T \left( \frac{\partial \ln q}{\partial T} \right)_V$$

where  $\ln(e) = 1$ . Stirling's approximation is  $\ln N! \simeq N \ln N - N$  for  $N \gg 1$ . [4]

- (b) By considering an atomic gas, and neglecting the electronic degrees of freedom, show that the translational contribution to  $S$  may be expressed in the form

$$\frac{S_{\text{tr}}}{Nk_B} = C + \frac{3}{2} \ln m$$

where  $m$  is the relative atomic mass, and  $C$  is independent of the chemical identity of the gas. [4]

The standard molar entropy of Ne at  $T=298$  K is  $S_m^\ominus = 146.2 \text{ J K}^{-1} \text{ mol}^{-1}$ . Determine  $S_m^\ominus$  for Ar at  $T=298$  K. Take the masses to be:  $m(\text{Ne}) = 20$ ,  $m(\text{Ar}) = 40$ . [2]

- (c) Assuming that only the ground and first excited electronic states are thermally accessible, show that the electronic contribution to the entropy is

$$\frac{S_{\text{el}}}{Nk_B} = \ln(g_0 + g_1 e^{-\beta\epsilon}) + \frac{\beta\epsilon g_1}{g_0 e^{\beta\epsilon} + g_1}$$

where  $\beta = 1/k_B T$ ,  $g_0$  and  $g_1$  are degeneracy factors and  $\epsilon$  is the energy of the excited electronic state relative to the ground state. [6]

Obtain the limiting values of  $S_{\text{el}}$  for  $k_B T \ll \epsilon$  and  $k_B T \gg \epsilon$ , and discuss the physical meaning of the results. [4]

- (d) Calculate the electronic contribution to the molar entropy of NO at  $T=298$  K. The energy separation between the ground and first excited electronic state of NO is  $121 \text{ cm}^{-1}$ , and  $k_B T/hc = 207.2 \text{ cm}^{-1}$  at  $T=298$  K. Comment on your answer. [4]

- (e) Obtain an expression for the rotational contribution to the entropy of NO. [4]

- (f) The total standard molar entropy of NO at  $T=298$  K is known to be  $S_m^\ominus = 210.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . Explain how this information could be used to estimate the bond length of NO, indicating any assumptions made. Detailed calculation is not required. [6]

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## 10. Atomic Spectroscopy

- (a) (i) Atomic wavefunctions are labelled with the quantum numbers  $n$ ,  $l$ , and  $m_l$ . Using the hydrogen atom for illustration, explain the meaning of each of these quantum numbers.

What is meant by a radial distribution function? Sketch on the same plot the radial distribution functions for the  $1s$ ,  $2s$  and  $2p$  hydrogenic orbitals. [7]

- (ii) The  $2p_z$  wavefunction in hydrogen is

$$\psi_{2p_z} = \frac{1}{4} \left( \frac{1}{a_0} \right)^{5/2} \left( \frac{1}{2\pi} \right)^{1/2} r \cos \theta e^{-r/2a_0}$$

Determine the radial distribution function, and show that the most probable radius of the electron in the  $2p_z$  orbital is  $r = 4a_0$ , where  $a_0$  is the Bohr radius. [8]

- (b) The following table shows effective nuclear charge values,  $Z_{\text{eff}}$ , for various electron configurations in lithium:

Configuration	$1s^2 2s^1$	$1s^2 2p^1$	$1s^2 3d^1$
$Z_{\text{eff}}$	1.259	1.020	1.000

Note that under the neglect of spin-orbit coupling, the energy levels of Li *relative to the ground state* are given by the expression

$$E_{nl} = I - \frac{\mathcal{R}Z_{\text{eff}}^2}{n^2} \quad \text{with} \quad \mathcal{R} = 1.097 \times 10^5 \text{ cm}^{-1}$$

where  $I$  is the ionization energy, and  $n$  is the principal quantum number associated with the valence electron.

- (i) Use the data to estimate the ionization energy of Li, and the energies of all the levels with respect to the ground state. You may leave your answer in units of  $\text{cm}^{-1}$ .  
(ii) Explain the variation of  $Z_{\text{eff}}$  with electron configuration. [10]

- (c) (i) In Li allowed electric dipole transitions occur between states arising from the  $1s^2 2s^1$  and  $1s^2 2p^1$  configurations, and between those arising from the  $1s^2 2p^1$  and  $1s^2 3d^1$  configurations, but transitions between states arising from the  $1s^2 2s^1$  and  $1s^2 3d^1$  configurations are forbidden. Provide a qualitative explanation for the origin of the selection rules that apply to these transitions.

- (ii) Discuss briefly the effect that a magnetic field would have on the states arising from the  $1s^2 2s^1$  and the  $1s^2 2p^1$  configurations. For Li atoms placed in a magnetic field, predict the number of lines that would be observed in transitions between states with these configurations. [9]

[You may use without proof the equation

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad ]$$

## 11. Nuclear magnetic resonance

(a) Discuss how NMR can be used to study *dynamic equilibria* ('chemical exchange') in molecules in solution. [6]

(i) What is meant by a 'free induction decay' in NMR? [3]

(ii) The free induction decay of an ensemble of identical nuclei with Larmor frequency  $\omega_0$  can be written in complex form as

$$M(t) = M_0 e^{i\omega_0 t} e^{-t/T_2}$$

where the magnetisation  $M_y$  is given by the real part of the expression and  $T_2$  is the transverse relaxation time.

The NMR spectrum,  $I(\omega)$ , is obtained by Fourier transformation of  $M(t)$  :

$$I(\omega) = C \operatorname{Re} \int_0^{\infty} M(t) e^{-i\omega t} dt$$

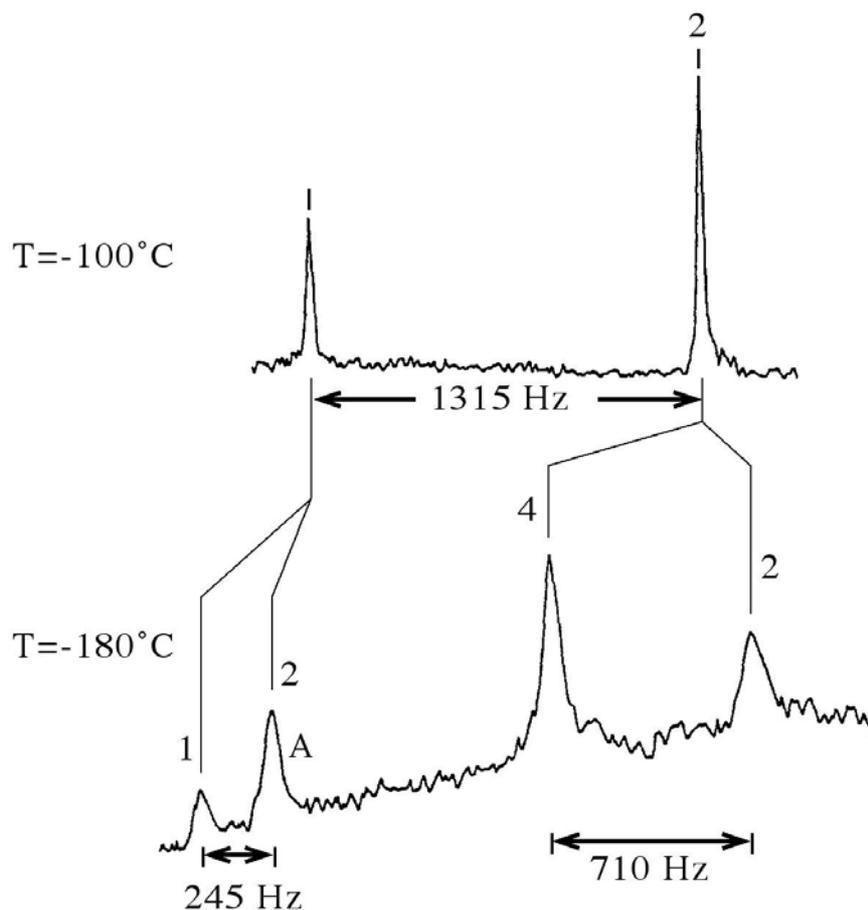
where  $C$  is a constant and 'Re' represents the real part of the expression that follows. Show that

$$I(\omega) = CM_0 \frac{\frac{1}{T_2}}{\left(\frac{1}{T_2}\right)^2 + (\omega - \omega_0)^2}$$

and hence that the full width at half maximum,  $\Delta\nu$ , of the peak is given by  $\Delta\nu = 1/\pi T_2$ . (Recall that  $\omega = 2\pi\nu$ .) [6]

(iii) How does the expression for  $\Delta\nu$  in (ii) assist in the determination of rate constants in dynamic equilibria? [3]

(b) The proton-decoupled  $^{13}\text{C}$ -NMR spectrum of liquid 2,3-dimethylbutane  $[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2]$  is shown on the next page at temperatures of  $-100^\circ\text{C}$  and  $-180^\circ\text{C}$ . The relative peak areas and the peak separations (in Hz) are indicated. You may assume that integrated peak areas are proportional to the number of spins in the sample.



1. (i) Assign the NMR peaks in the spectrum acquired at  $-100\text{ }^{\circ}\text{C}$  and explain why more peaks are observed in the spectrum at  $-180\text{ }^{\circ}\text{C}$  than at  $-100\text{ }^{\circ}\text{C}$ . [4]
- (ii) By carefully considering the different rotational conformers in 2,3-dimethylbutane, assign the peaks at  $-180\text{ }^{\circ}\text{C}$  and determine the relative populations of the different conformers. (Note that not all the peaks are fully resolved.) [7]
- (iii) The linewidth of the peak labelled 'A' at temperatures sufficiently low that chemical exchange is insignificant is  $\Delta\nu = 71\text{ Hz}$ ; at  $-178\text{ }^{\circ}\text{C}$ ,  $\Delta\nu = 125\text{ Hz}$ . Estimate the rate constant,  $k$ , at  $-178\text{ }^{\circ}\text{C}$  for the exchange process you have identified in (ii) above and hence calculate the activation free energy,  $\Delta G^{\ddagger}$ . [5]

## 12. Photochemistry/Reaction Dynamics

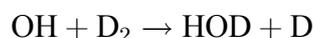
- (a) Draw a molecular orbital (MO) diagram for the OH radical, and use it to predict the ground electronic state of the radical. In drawing your diagram you need only consider the  $2p$  levels of oxygen, which you can assume lie lower in energy than the H atom  $1s$  orbital. [5]
- (b) In the gas phase, the OH radical in its ground electronic state is often detected by observing fluorescence induced by laser excitation to the lowest excited state, which has  $^2\Sigma$  symmetry. Use your MO diagram to identify the likely electronic configuration of this excited state. [4]
- (c) Explain briefly what is meant by vibrational predissociation.  $\text{OH}(^2\Sigma)$  undergoes predissociation above the vibrational level  $v' = 1$ , which becomes increasingly rapid with increasing  $v'$ . What effect would this predissociation have on the fluorescence quantum yield, the observed fluorescence lifetime, and the linewidths of resolved rovibronic transitions? [6]
- (d) How would you expect the linewidths of transitions to levels with  $v' \leq 1$  to vary with temperature and total pressure? Explain your reasoning. [4]
- (e) Electronically excited  $\text{OH}(^2\Sigma)$  also undergoes rapid electronic quenching with certain molecules. How does the presence of a quencher gas affect the observed fluorescence rate constant?

The following table shows  $\text{OH}(^2\Sigma)$   $v' = 0$ , observed fluorescence lifetimes,  $\tau_{\text{obs}}$ , as a function of water concentration. Employ a graphical procedure to obtain the quenching rate constant for  $\text{OH}(^2\Sigma)$  with water, and its radiative lifetime in the  $v' = 0$  vibrational level.

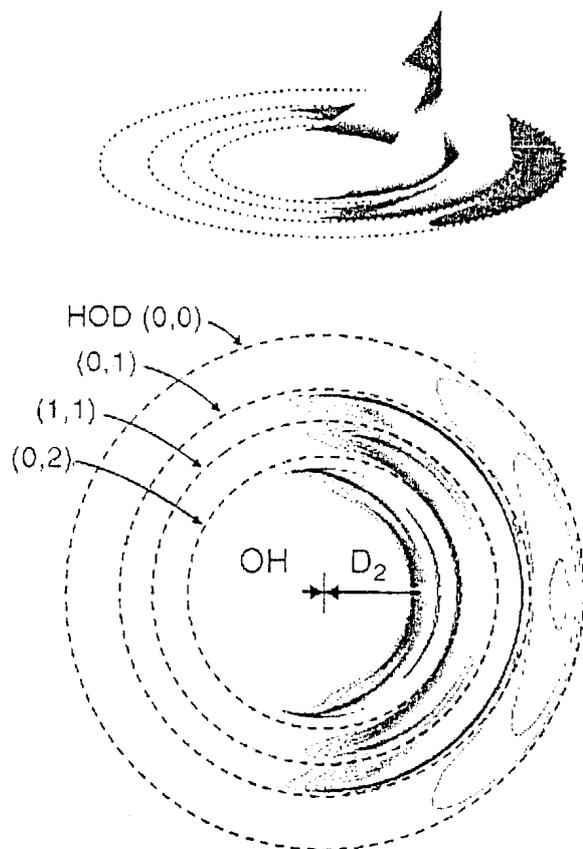
$[\text{H}_2\text{O}]/(10^{15} \text{ molecule cm}^{-3})$	0.5	1.0	1.5	2.0	2.5
$\tau_{\text{obs}}/\text{ns}$	710	620	540	490	440

How would you expect the quenching rate constant to compare qualitatively with that for  $\text{OH}(^2\Sigma)$  with a rare gas? [8]

- (f) OH in its ground electronic state undergoes the reaction



which is isoelectronic with the  $\text{F} + \text{H}_2$  reaction. The figures below show plots of product flux in the centre-of-mass frame for the above reaction. The experiments were performed under molecular beam conditions, with the D atom products detected by a laser ionization technique.



The dashed rings are labelled according to the number of quanta  $m$  in the bending mode, and  $n$  in the OD stretching mode of  $\text{HOD}(m, n)$ .

- (i) What does the above figure suggest about the mechanism of the reaction?
- (ii) What spectroscopic experiments might be performed to probe the transition state region of this reaction (or a similar reaction) more directly?

[7]

### 13. Polymers

(a) Discuss simple models for rationalising the conformation of an isolated polymer chain in solution. Points that you may wish to address include

random walk model  
equivalent freely jointed links  
excluded volume  
Flory radius  
Flory-Huggins Model  
good, theta and poor solvents

(Note: Mathematical derivations are not expected)

[16]

(b) A polymer brush is characterised by four parameters:

$N$  - the number of monomers per chain  
 $a^3$  - the volume per monomer  
 $L$  - the thickness of the brush  
 $\Gamma (=1/s^2)$  - the number of chains per unit area.

(i) Explain what is meant by a ‘polymer brush’. [3]

(ii) The osmotic pressure,  $\Pi$ , in the semi-dilute regime scales as  $\frac{k_B T}{a^3} \phi^2$ , where  $\phi$  is the volume fraction. Write down a scaling expression for the osmotic pressure in the brush. [3]

(iii) The free energy of stretching of a polymer chain scales as  $\frac{L^2}{Na^2} k_B T$ . How does the stretching force *per unit area* of the surface scale with  $N$ ,  $a$ ,  $L$ , and  $\Gamma$ ? [4]

(iv) By balancing the osmotic and stretching pressures on the brush, determine how  $L$  scales with  $N$ ,  $a$  and  $s$ . [3]

(v) Comment on the exponent of  $N$  in light of the scaling behaviour in solution. [2]

(vi) What effect do polymer brushes have on the stability of colloids? [3]