

DCHA 2713

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Tuesday, 8th June 1999, 9.20 a.m. to 12.30 p.m.

Candidates should answer *three* questions

The marks in square brackets indicate the weight the examiners expect to assign to each part of the question.

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Speed of light, $c$	=	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant, $h$	=	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, $k_B$	=	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant, $R$	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant, $N_A$	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
1 M	=	$1 \text{ mol dm}^{-3}$
$p^\ominus$	=	$1 \text{ bar} = 10^5 \text{ Pa}$
1 atm	=	$101.325 \text{ kPa} = 760 \text{ Torr}$
Elementary charge, $e$	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, u	=	$1.661 \times 10^{-27} \text{ kg}$
Faraday constant, $F$	=	$9.6487 \times 10^4 \text{ C mol}^{-1}$
1 Da	=	$1 \text{ g mol}^{-1}$
Vacuum permittivity $\epsilon_0$	=	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Electron mass, $m_e$	=	$9.109 \times 10^{-31} \text{ kg}$
$V_m^\ominus$	=	$24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K

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1. Nuclear magnetic resonance
2. Surfaces
3. Dynamic electrochemistry
4. Atomic and molecular spectroscopy
5. Thermodynamics
6. Valence theory, spectroscopy, group theory
7. Statistical thermodynamics
8. Theories of Kinetics
9. Reaction dynamics and Unimolecular Reactions
10. Quantum mechanics
11. Molecular interactions I
12. Molecular interactions II

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Turn over

1. The nuclear spin energy levels (expressed as frequencies) of molecule **1** in a magnetic field are as follows:

	$m_H$	$m_D$	frequency/Hz
1.	-1/2	-1	+261 457 945
2.	-1/2	0	+200 000 000
3.	-1/2	+1	+138 542 055
4.	+1/2	-1	-138 542 057
5.	+1/2	0	-200 000 000
6.	+1/2	+1	-261 457 943

You may assume that both carbons are  $^{12}\text{C}$  and that X is non-magnetic. D denotes deuterium.

(a) Explain the significance of the symbols  $m_H$  and  $m_D$ , and state the appropriate NMR selection rules. [3]

(b) By calculating the frequencies of the allowed transitions determine:

- (i) the H-D spin-spin coupling constant;
- (ii)  $\gamma_H/\gamma_D$ , the ratio of the gyromagnetic ratios of the two isotopes;
- (iii) the strength of the magnetic field in Tesla ( $\gamma_H = 2.675 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$ )

[6]

(c) Sketch the appearance of the proton and deuterium NMR spectra of molecule **1**, carefully justifying the relative intensities of the transitions in each spectrum. Which spectrum would you expect to be more intense, and why? [4]

(d) Explain as fully as possible the effect on the two spectra of replacing both X substituents by chlorine atoms. ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  both have  $I = 3/2$ ). [4]

(e) How and why would the proton spectrum of molecule **2** differ from that of molecule **1**? Estimate the  $^1\text{H}$ - $^1\text{H}$  spin-spin coupling constant in molecule **2**. [4]

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Question continues

(f) The one-bond  $^{13}\text{C}$ - $^1\text{H}$  spin-spin coupling constant in ethene is  $\sim 167$  Hz. The corresponding quantities for ethane and ethyne are  $\sim 125$  and  $\sim 250$  Hz. Comment on these values in the context of the mechanism of the spin-spin coupling. [3]

(g) Sketch the appearance of the  $^{13}\text{C}$  NMR spectrum of molecule **3**. [2]

(h) The spin Hamiltonian of  $^{12}\text{CHF}_2\text{Cl}$  (ignoring the fluorine Zeeman interaction, the F-F spin-spin coupling, and the chlorine atom) may be written as:

$$\hat{H} = -\nu_{\text{H}}\hat{I}_{\text{Hz}} + J_{\text{HF}}(\hat{I}_{\text{Hz}}\hat{I}_{\text{F1z}} + \hat{I}_{\text{Hz}}\hat{I}_{\text{F2z}})$$

where  $\nu_{\text{H}}$  is the proton Larmor frequency, and  $J_{\text{HF}}$  is the H-F spin-spin coupling constant.  $\hat{I}_{\text{Hz}}$ ,  $\hat{I}_{\text{F1z}}$  and  $\hat{I}_{\text{F2z}}$  are the  $z$ -components of the spin angular momentum operators of the proton, and the two fluorine nuclei.

Obtain expressions for the energy levels of the HFF spin system, and the frequencies of the allowed transitions in the proton NMR spectrum, and hence demonstrate that the  $^1\text{H}$  signal is a triplet. [8]

**2.** Describe the following techniques and explain how each provides information about solid surfaces.

- (i) Scanning tunnelling and atomic force microscopies,
- (ii) X-ray photoelectron and Auger spectroscopies,
- (iii) Low energy electron diffraction. [15]

The dissociative sticking probability,  $S$ , of oxygen on Cu(110) was measured at two different temperatures. The data indicated a linear decrease in  $S$  with coverage,  $\theta$ , at each temperature:

$$S = S_0(1 - 2\theta)$$

where  $S_0 = 0.22$  at 300 K and  $S_0 = 0.45$  at 850 K. A LEED pattern, shown below, was also observed at low coverages and attained maximum intensity at a coverage of exactly 0.5 monolayers.

(a) Calculate the activation energy for dissociative adsorption. [4]

(b) Interpret the LEED pattern suggesting a structure for the Cu(110) surface and for the overlayer. [5]

(c) Contrast the observed dependence of  $S$  on  $\theta$  with that assumed in deriving the Langmuir isotherm for dissociative adsorption. Suggest an explanation for the observed dependence noting that the LEED pattern from the overlayer is present even at low coverage. [4]

(d) How long would it take for 0.05 monolayers of oxygen to adsorb on the surface at  $1.0 \times 10^{-9}$  Torr at 300 K given that the lattice constant of copper is 361 pm, and assuming that the sticking probability varies negligibly with coverage over the range of interest? The rate of surface bombardment per unit area by molecules ( $Z$ ) is given by

$$Z = \frac{p}{(2\pi mk_B T)^{\frac{1}{2}}}$$

where  $p$  is the pressure,  $k_B$  is the Boltzmann constant and  $m$  is the molecular mass. The relative atomic mass of oxygen is 16. [6]

3. Answer **all** parts.

A. Write an account of cyclic voltammetry. Include a detailed description of the form of the current-voltage curve seen for the process



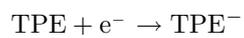
when both Ox and Red are stable. Explain what is seen if Red is unstable and how the kinetics of its decay could be investigated. Illustrate how cyclic voltammetry is used to obtain information about electrode reaction mechanisms. [16]

B. The figures below show cyclic voltammograms of fac-Mn(CO)<sub>3</sub>dpmCl (dpm = Ph<sub>2</sub>PCH<sub>2</sub>P Ph<sub>2</sub>) in acetonitrile solution at (a) 22°C and (b) -35°C. In (a) the dotted curve represents the first cycle and the solid curve the second and subsequent cycles. *Note that each potential cycle starts near +0.5 V and sweeps first in a positive direction as shown by the arrow. Anodic (oxidation) currents are shown as negative; cathodic (reduction) currents as positive.* Suggest an interpretation of the voltammograms. [9]

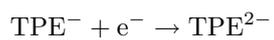
C. Explain how the peak-to-peak separation in a cyclic voltammogram can give information about whether the heterogeneous electron transfer between the electrode and the solution phase species is fast or slow. Comment on **three** of the following statements invoking Marcus theory where appropriate.

- (i) The Anthracene/Anthracene<sup>-</sup> couple has a very fast standard electrochemical rate constant of *ca* 4 cm s<sup>-1</sup>.
- (ii) The oxidation of carboxylate anions (RCO<sub>2</sub><sup>-</sup>) at platinum electrodes requires a very large overpotential.
- (iii) The Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> /Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> couple shows exceptionally slow electrode kinetics.

(iv) In non-aqueous solvents tetraphenylethene (TPE,  $\text{Ph}_2\text{C}=\text{CPh}_2$ ) undergoes reduction to the monoanion and the dianion in two separate voltammetric steps. The rate constant for



is almost two orders of magnitude greater than for



[9]

4. Answer **two** of the following three parts

**A.** Predict the ordering of the lowest four excited terms of the helium atom which arise from excitation of one electron into the  $n = 2$  shell. Include in your answer a discussion of the following; *Russell-Saunders coupling, Hund's rules, electron spin correlation, effective nuclear charge.* [9]

Explain why some of these excited states are metastable with respect to decay to the ground state and comment on the relevance of this metastability to the mechanism for population inversion in the helium-neon laser.

Transitions of the type  $1s^2 \rightarrow 2s^1 2p^1$  have been observed for the helium atom. Comment on this observation in the context of *configuration interaction.* [8]

**B.** The *vibrational* Raman spectrum of  $D_2$  shows Stokes lines at the following displacements from the exciting line

Displacement/cm <sup>-1</sup>
3390.0
3278.0
3164.8
2812.5
2690.7
2566.8

A broad central peak is also observed at approximately 2990 cm<sup>-1</sup>.

Draw an energy level diagram to illustrate the observed transitions.

Using the method of combination differences, or otherwise, determine values of the rotational constants  $B_0$ ,  $B_1$  and  $B_e$ , and the equilibrium bond length for  $D_2$  (you may ignore centrifugal distortion). Explain whether you would expect the equilibrium bond length for  $H_2$  to differ from this value. [10]

The vibrational Raman spectrum of the  $D_2$  molecule shows an 'intensity alternation'. Write down the complete set of nuclear spin wavefunctions for this molecule (for the deuterium nucleus,  $I=1$ ) and use these to explain the intensity alternation. Predict the relative intensities at 300 K of the first three lines in the S branch of the Raman spectrum listed above (You may ignore the rotational dependence of the transition moment.)

$$hc/k_B T = 4.795 \times 10^{-3} \text{ cm at 300 K}$$

The relative atomic mass of deuterium is 2. [7]

**C.** The rotational energy of a three-dimensional body is given in classical mechanics by the expression:

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

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where  $J_a$ ,  $J_b$  and  $J_c$  are components of the total angular momentum about three perpendicular axes through the centre of mass of the body, and  $I_a$ ,  $I_b$ ,  $I_c$  are moments of inertia about those axes.

Starting from the classical energy expression, show that the following energy level formulae may be deduced

(i) For a spherical top molecule ( $I_a = I_b = I_c$ ) :  $E/hc = BJ(J+1)$

(ii) For a prolate symmetric top molecule ( $I_a < I_b = I_c$ ):  $E/hc = BJ(J+1) + (A-B)K^2$

where  $B = h/8\pi^2 I_b c$  and  $A = h/8\pi^2 I_a c$

What does the quantum number  $K$  represent, and what range of values can it take for a given  $J$ ?

Sketch an energy level diagram for a prolate symmetric top molecule ( $I_a < I_b = I_c$ ) for values of  $J$  up to 2, and indicate the quantum numbers and degeneracies of each level.

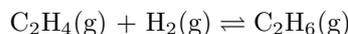
Predict the appearance of the rotational spectrum of a prolate symmetric top molecule on the basis of the energy level formula given above. [11]

The through-space H-H distance in the symmetric top molecule  $\text{CH}_3\text{F}$  is 182 pm. Calculate a value for the  $A$  rotational constant in this molecule. [6]

The relative atomic mass of hydrogen is 1.

**5. Answer all parts**

**A.** The reaction enthalpy and entropy of the gas phase reaction



are  $\Delta_r H^\circ = -137.0 \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ = -120.5 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K. In the temperature range 298 - 1000 K, the difference in molar heat capacities of products and reactants is

$$\Delta_r C_p^\circ / (\text{J K}^{-1} \text{ mol}^{-1}) = -27.2 + 0.0256(T/\text{K}).$$

(a) Calculate  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  at 1000 K and hence show that the equilibrium constant  $K_p = 2.92$  at 1000 K.

(b) 1 mol  $\text{C}_2\text{H}_4(\text{g})$  and 1 mol  $\text{H}_2(\text{g})$  are mixed at 1 bar total pressure and 1000 K.

(i) Determine the number of moles of ethane present at equilibrium at 1 bar.

(ii) What total pressure would be needed for the mole fraction of ethane at equilibrium to be 0.99 at 1000 K? [14]

**B.** 10 g of solid  $\text{CaCO}_3$  is sealed in an evacuated container (volume  $10 \text{ dm}^3$ ) at 1000 K and allowed to come to equilibrium according to the equation:



(a) What mass of  $\text{CaCO}_3$  remains at equilibrium? Assume that  $\text{CO}_2$  behaves ideally.  $\Delta_r G^\circ = +23.5 \text{ kJ mol}^{-1}$  at 1000 K. Relative atomic masses: C 12, O 16, Ca 40.

(b) A small quantity of  $\text{CaO}$  is sealed in a vessel containing a large excess of  $\text{CO}_2$  at 1 bar. Discuss the equilibrium composition in the temperature range 1000–1200 K. Assume that  $\Delta_r H^\circ$  ( $178 \text{ kJ mol}^{-1}$ ) and  $\Delta_r S^\circ$  are independent of temperature. [10]

**C.** (a) Give the expression for the chemical potential of a component in an ideal solution.

(b) Two compounds A and B form an ideal solution when liquid, but are totally immiscible as solids. Show that if A and B have identical enthalpies of fusion ( $\Delta_{\text{fus}} H^\circ$ ), then the mole fraction of A at the eutectic point is given by

$$\ln \left( \frac{x_A}{1 - x_A} \right) = \frac{\Delta_{\text{fus}} H^\circ}{R} \left( \frac{1}{T_A} - \frac{1}{T_B} \right)$$

where  $T_A$  and  $T_B$  are the melting points of the two compounds.

(c) Determine the composition and temperature of the eutectic mixture from the following data:

$$\Delta_{\text{fus}}H^\ominus = 10.0 \text{ kJ mol}^{-1} \quad T_A = 320 \text{ K} \quad T_B = 370 \text{ K}$$

Sketch the phase diagram.

[10]

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**6.**

(a) Discuss what is meant by the *orbital approximation* in the context of the theory of molecular bonding. [4]

(b) Consider the six  $p_z$  orbitals on the carbon atoms of the benzene ring that overlap to provide the conjugated  $\pi$  system in this molecule. Using group theory, show that the symmetrised linear combinations of these orbitals consist of two singly degenerate molecular orbitals and two doubly degenerate pairs. (Benzene belongs to the point group  $D_{6h}$ , with  $C_2'$  axes passing through two carbon atoms, and the  $C_2''$  between carbon atoms).

Each orbital may be written in the form

$$\Psi_i = \sum_j c_{ij} \phi_j$$

where  $\phi_j$  is an atomic  $p_z$  orbital on atom  $j$ .

Use group theory to deduce the coefficients for both of the singly degenerate orbitals and for one of each of the doubly degenerate pairs. [12]

Using the approximations of Hückel theory, calculate the orbital energies for each of the four orbitals.

Illustrate the orbital occupancy in the ground state of benzene on an orbital energy diagram and deduce the term symbol for the ground state. [10]

(c) The lowest excited states of benzene are obtained by exciting one electron from the HOMO to the LUMO. Deduce the term symbols of these excited states and determine which of the excitations are fully allowed electronic transitions. [4]

The  $S_1$  state of benzene has a relatively low transition intensity from the ground state and the band origin corresponding to the transition between the zero-point levels of the  $S_0$  and  $S_1$  states is missing from the spectrum. The first feature observed corresponds to simultaneous vibrational excitation of one quanta of a mode of  $e_{2g}$  symmetry.

Is it possible to identify the symmetry of the  $S_1$  state out of the possible terms deduced above? [4]

**7.** A solid contains ions with a magnetic moment due to angular momentum  $J = 1$ . Electric effects within the solid cause the states with  $m_J = \pm 1$  to have an energy lower by  $\Delta$  than the state with  $m_J = 0$ . A magnetic field  $B$  is applied such that the  $m_J = \pm 1$  states shift in energy by  $\pm g_J \mu_B B$  ( $\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$ ). Assume that  $g_J = 4/3$ .

(a) Comment on the temperature dependence of the molar internal energy  $U_m$  shown below for:

- (i)  $B = 0, \Delta/k_B = 50 \text{ K}$ ;
- (ii)  $B = 2.23 \text{ T}, \Delta/k_B = 50 \text{ K}$ ;

Sketch the temperature dependence of the molar heat capacity  $C_{V,m}$  for the two cases over the temperature range  $0 - 80 \text{ K}$ . [8]

(b) Under what conditions of temperature and field would the molar entropy equal:

- (i)  $R \ln 2$ ; (ii)  $R \ln 3$ ? [4]

(c) Obtain an expression for the total magnetization  $M$  when  $g_J \mu_B B \ll k_B T$  and hence for the magnetic susceptibility  $\chi$ , defined as  $M/B$  in the limit  $B \rightarrow 0$ . The magnetization is given by

$$M = -N g_J \mu_B \sum_{m_J} m_J P_{m_J}$$

where  $P_{m_J}$  is the fraction of the total number of ions  $N$  in level  $m_J$ . [10]

(d) Show that Curie's Law is obeyed (i.e.  $\chi \propto 1/T$ )

when (i)  $k_B T \gg \Delta$ ,

and when (ii)  $k_B T \ll \Delta$ ,

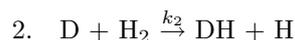
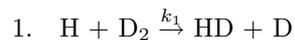
but not when (iii)  $k_B T \approx \Delta$ . [6]

(e) Show that the ratio of the Curie constants in cases (i) and (ii) above is  $2/3$ . Explain this result in simple terms. [6]

8. (a) Explain what is meant by *kinetic isotope effect* and how it is related to zero point energy.

[4]

(b) Consider the following gas-phase reactions:



Estimate the ratio of the rate constants  $k_2/k_1$  at 300 K using the vibrational wavenumbers given below. Assume that the effect of isotopic substitution is limited to changes in the zero point energies of reactants and transition states, and that the transition states are linear.

	H <sub>2</sub>	Reaction 1 Transition state	Reaction 2 Transition state
Stretch (cm <sup>-1</sup> )	4395	1762	1773
Bend (doubly degenerate) (cm <sup>-1</sup> )	-	694	870

(1 cm<sup>-1</sup> ≡ 11.96 J mol<sup>-1</sup>)

[8]

(c) For the reaction of an atom X with a diatomic molecule Y<sub>2</sub>



proceeding through a linear transition state, Transition State Theory gives

$$k = \frac{k_B T}{h} \frac{q_{int}^\ddagger}{q_t q_{X:int} q_{Y_2:int}} e^{-\varepsilon_0/k_B T}$$

where  $q_{X:int}$  and  $q_{Y_2:int}$  are the partition functions for the internal modes (rotational, vibrational, electronic) of the reactants and  $q_t$  is related to the masses of the reactants by

$$q_t = \left( \frac{2\pi k_B T}{h^2} \frac{m_X m_{Y_2}}{m_X + m_{Y_2}} \right)^{3/2}$$

Outline the origin of the expression for  $k$  (no derivations are required), comment on the assumptions involved, and explain the meaning of the symbols  $q_{int}^\ddagger$  and  $\varepsilon_0$ .

[8]

(d) Show that the expression for  $k$  in (c) leads to the following equation, stating and justifying the assumptions and approximations used.

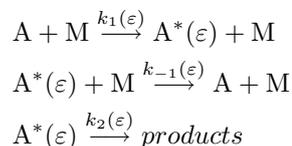
$$\frac{k_2}{k_1} = \frac{m_D}{m_H} \frac{I_2^\ddagger}{I_1^\ddagger} \left( \frac{m_D + 2m_H}{m_H + 2m_D} \right)^{3/2} \exp[-(\varepsilon_{0:2} - \varepsilon_{0:1})/k_B T]$$

The 1,2 subscripts refer to the two reactions in (b) and  $I^\ddagger$  denotes the moment of inertia of the transition state. [8]

(e) Hence obtain a revised estimate of  $k_2/k_1$  at 300 K. ( $I_1^\ddagger = 4.02 \times 10^{-47}$  kg m<sup>2</sup>,  $I_2^\ddagger = 3.95 \times 10^{-47}$  kg m<sup>2</sup>; the relative atomic masses of H and D are 1 and 2 respectively). [3]

(f) The experimental value of  $k_2/k_1$  is 14 at 300 K. Why is this value larger than that predicted by Transition State Theory? [3]

9. (a) The RRK model for unimolecular reactions uses an energy dependent version of the Lindemann reaction scheme:



The rate constants are given by the following expressions.

$$\frac{k_1(\varepsilon)}{k_{-1}(\varepsilon)} = \frac{1}{(s-1)!} \left( \frac{\varepsilon}{k_B T} \right)^{(s-1)} e^{-\varepsilon/k_B T}$$

$$k_2(\varepsilon) = \nu \left( \frac{\varepsilon - \varepsilon_0}{\varepsilon} \right)^{s-1}$$

- (i) Discuss the meaning of the quantities,  $\varepsilon$ ,  $\varepsilon_0$ ,  $s$  and  $\nu$  in the theory.
- (ii) How can the rate constant  $k_{-1}(\varepsilon)$  be estimated?
- (iii) Derive an expression for the overall temperature dependent rate constant  $k_{\text{uni}}(T)$ .
- (iv) How would the quantities  $k_1(\varepsilon)/k_{-1}(\varepsilon)$  and  $k_2(\varepsilon)$  change as  $s$  increases and as  $\varepsilon$  increases?

Explain the physical reasons for this behaviour. [14]

The following data have been obtained for  $k_2(\varepsilon)$  as a function of  $\varepsilon$  for isomerisation of cyclobutene. In this case  $\varepsilon_0$  is estimated to be  $139 \text{ kJ mol}^{-1}$  and  $\nu$  is determined to be equal to  $5.75 \times 10^{13} \text{ s}^{-1}$ .

$\varepsilon/\text{kJ mol}^{-1}$	162	170	180	187	197
$k_2(\varepsilon)/\text{s}^{-1}$	$3 \times 10^7$	$9 \times 10^7$	$2 \times 10^8$	$5 \times 10^8$	$8 \times 10^8$

- (v) What value would be obtained for  $k_2(\varepsilon)$  as  $\varepsilon \rightarrow \infty$ ?
- (vi) Using your answer to (v) and the data in the table above, devise a graphical procedure to test the validity of the RRK model. To what extent is it possible to determine a value for  $s$ ?
- (vii) What are the major deficiencies of the RRK model? [9]

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

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(b) Explain what is meant by the *potential energy surface* for a reaction and illustrate your answer with respect to a reaction of the type  $A + BC \rightarrow AB + C$ . What effect does the shape of the potential energy surface have on the distribution of excess energy in the reaction? What other factors are important?

The figures below show the product flux contour plots in the centre of mass frame (CM) of three different reactions.

What can be learnt about the dynamics of these reactions from the figures?[11]

The dashed circles show the maximum product velocity.

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10. (a) Consider an harmonic oscillator with the Hamiltonian

$$\hat{H}_0 = \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

(i) Show that the operators

$$\hat{Q}^- = \sqrt{\frac{1}{2}} \left[ \frac{\hbar}{\sqrt{\mu}} \frac{d}{dx} + \sqrt{k}x \right] \quad \text{and} \quad \hat{Q}^+ = \sqrt{\frac{1}{2}} \left[ -\frac{\hbar}{\sqrt{\mu}} \frac{d}{dx} + \sqrt{k}x \right]$$

satisfy

$$\hat{Q}^+ \hat{Q}^- + \frac{1}{2} \hbar \omega = \hat{H}_0 \quad \text{and} \quad \hat{Q}^- \hat{Q}^+ - \frac{1}{2} \hbar \omega = \hat{H}_0$$

where  $\omega = \sqrt{k/\mu}$ . Use these relations to show also that

$$\hat{H}_0 \hat{Q}^+ = \hat{Q}^+ (\hat{H}_0 + \hbar \omega)$$

and

$$\hat{H}_0 \hat{Q}^- = \hat{Q}^- (\hat{H}_0 - \hbar \omega)$$

(ii) Using these relations, show that if  $\Psi_n$  is an eigenfunction of  $\hat{H}_0$  with eigenvalue  $E_n$  then  $\hat{Q}^+ \Psi_n$  is an eigenfunction of  $\hat{H}_0$ , notated  $\Psi_{n+1}$  with eigenvalue

$$E_{n+1} = E_n + \hbar \omega.$$

Show similarly that  $\hat{Q}^- \Psi_{n+1}$  is an eigenfunction with eigenvalue  $E_{n+1} - \hbar \omega = E_n$ .

(iii) By expressing  $x$  in terms of  $\hat{Q}^-$  and  $\hat{Q}^+$  evaluate the form of the matrix elements

$$\langle \Psi_n | x | \Psi_{n+1} \rangle \quad \text{and} \quad \langle \Psi_n | x | \Psi_{n+2} \rangle$$

Discuss the relevance of the matrix elements to infrared spectroscopy. [18]

(b) A truer representation for the potential of a diatomic molecule might be of the form

$$V(x) = \frac{1}{2} kx^2 - ax^3$$

where  $x = R - R_e$  is the displacement of the internuclear distance from equilibrium, so that the Hamiltonian may be written

$$\hat{H} = \hat{H}_0 - ax^3$$

**Question continues**

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**Turn over**

In the variation principle a trial wavefunction of the form

$$\Psi(x) = \frac{1}{(1+b^2)^{1/2}} (\Psi_0(x) + b\Psi_1(x))$$

may be used where

$$\begin{aligned}\Psi_0 &= \left(\frac{c}{\pi}\right)^{1/4} e^{-cx^2/2} \\ \Psi_1 &= \left(\frac{4c^3}{\pi}\right)^{1/4} xe^{-cx^2/2}\end{aligned}$$

are the exact normalised eigenfunctions for a harmonic oscillator in  $v = 0$  and 1.

Using the following matrix elements without proof

$$\begin{aligned}\langle \Psi_0 | \hat{H} | \Psi_0 \rangle &= \frac{1}{2}\hbar\omega \\ \langle \Psi_1 | \hat{H} | \Psi_1 \rangle &= \frac{3}{2}\hbar\omega \\ \langle \Psi_0 | \hat{H} | \Psi_1 \rangle &= -\frac{1}{2}\gamma\end{aligned}$$

where

$$\gamma = \frac{3\sqrt{2}a}{c^{3/2}}$$

use the variation principle to show that the best possible wavefunction, has a mixing coefficient  $b$  given by the solution of the quadratic equation:

$$b^2 + \left(\frac{2\hbar\omega}{\gamma}\right)b - 1 = 0$$

[16]

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11. (a) Explain the terms, *critical temperature* and *Boyle temperature*. [6]

(b) Consider a Van der Waals gas which obeys the following equation

$$\left(p + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

where  $p$  is pressure,  $V_m$  is the molar volume and  $T$  is the temperature.

(i) Account for the form of the Van der Waals equation. [4]

(ii) Noting that at the critical point there is a point of inflexion in the  $pV$  isotherm show that the molar volume at the critical point is  $V_c = 3b$ . Likewise show that the critical pressure  $p_c = a/27b^2$ . Deduce an expression for the critical temperature,  $T_c$ , in terms of  $a$ ,  $b$  and  $R$  and hence show that

$$\frac{RT_c}{p_c V_c} = \frac{8}{3}$$

[8]

(iii) Rewrite the Van der Waals equation in terms of the reduced variables

$$p_R = \frac{p}{p_c} ; T_R = \frac{T}{T_c} ; V_R = \frac{V_m}{V_c}$$

Comment on your result. [6]

(iv) For He, the parameters  $a$  and  $b$  have the values  $3.41 \times 10^4 \text{ cm}^6 \text{ atm mol}^{-2}$  and  $23.7 \text{ cm}^3 \text{ mol}^{-1}$  respectively. Estimate values of  $p_c$  and  $V_c$  for He. [2]

(v) By considering binary collisions between hard sphere molecules and the volume unavailable to the centres of both molecules derive an expression relating  $b$  to the molecular diameter  $d$ . Hence, by using the data in (iv), estimate the radius of a He atom. [4]

(vi) By recasting the Van der Waals equation in the form of the virial equation,

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

or otherwise, show that for a Van der Waals gas, the Boyle temperature is given by

$$T_B = \frac{a}{Rb}$$

Sketch and explain the variation of the product  $pV$  with  $p$  at temperatures above and below the Boyle temperature. [4]

12. Answer **both** parts.

(a) Write notes about surfactants and micelles giving chemical examples. Explain the term *critical micelle concentration* and how it may be determined. What is the *Kraft temperature*? [7]

(b) (i) Explain carefully the terms *surface excess concentration*,  $\Gamma$ , and *surface tension*,  $\gamma$ . [7]

(ii) Using the Gibbs equation  $d\gamma = -\Gamma RT d(\ln c)$  calculate the surface excess concentration of butan-1-ol in a 0.1000 M aqueous solution if molar concentrations and surface tensions of such solutions are as follows at  $T = 298$  K

$c/\text{mol dm}^{-3}$	0.01320	0.0264	0.0536	0.1050	0.2110	0.4330
$\gamma/\text{mN m}^{-1}$	70.82	68.00	63.14	56.31	48.08	38.87

What is the area occupied by one molecule of butan-1-ol at the surface? [12]

(iii) When the surface tension of aqueous solutions of 1,3-dihydroxybenzene are plotted as a function of the (natural) logarithm of the molar concentration of the solution, the graph is linear from 0.1 M to 10 M at 20°C. The constant slope of this plot is  $-3.5 \text{ mN m}^{-1}$ . Contrast this observation with the behaviour in (ii) and discuss possible explanations. [8]