

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ADVANCED PHYSICAL CHEMISTRY

Tuesday, 5th June 2001, 2.20 p.m. to 5.30 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.

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

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

1. *Magnetic resonance*
2. *Theories of kinetics*
3. *Molecular interactions: colloids*
4. *Reaction dynamics*
- 5A. *Vibrational spectroscopy: group theory*
- 5B. *Quantum mechanics*
6. *Molecular interactions: polymers*
- 7A. *Molecular spectroscopy*
- 7B. *Valence*
8. *Enzyme kinetics*
- 9A. *Thermodynamics*
- 9B. *Statistical mechanics*
10. *Surfaces*
11. *Dynamic electrochemistry*

Fundamental Constants

Speed of light	c	$2.997 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant	k	$1.381 \times 10^{-23} \text{ J K}^{-1}$
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	$1.602 \times 10^{-19} \text{ C}$
Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	m_p	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	ϵ_0	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Atomic mass unit	u	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$

Other Conventions

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

1. Magnetic resonance

(a) A sample of $^{13}\text{CCl}_4$ is placed in a 400 MHz NMR spectrometer. Once thermal equilibrium has been established, the populations of the two ^{13}C states are n_α^{eq} and n_β^{eq} .

(i) Estimate the ^{13}C NMR frequency using the following data. [2]

$$\gamma_H = +2.675 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$$

$$\gamma_C = +6.73 \times 10^7 \text{ T}^{-1}\text{s}^{-1}$$

(ii) Show that, to a very good approximation, the population difference ($n_\alpha^{eq} - n_\beta^{eq}$) is proportional to the Larmor frequency for ^{13}C nuclei at room temperature. You may wish to use $\exp(-x) \simeq 1 - x$. [4]

(b) When a sample of liquid $^{13}\text{CHCl}_3$ is first placed in the magnetic field of an NMR spectrometer, the two ^{13}C populations, n_α and n_β , are essentially identical. It can take several seconds for the equilibrium population difference to be established.

(i) Comment as fully as possible on these observations. [4]

(ii) Why did ^{13}C NMR take much longer than ^1H NMR to become a routine tool in chemistry? [4]

(iii) Predict the appearance of the proton-decoupled ^{13}C NMR spectrum of a sample of liquid $\text{C}_2\text{H}_5\text{Cl}$ in which the ^{13}C has been uniformly enriched to 50%. [Proton decoupling removes the splittings that arise from interactions between ^{13}C and ^1H .] [4]

(iv) Why does ^{13}C NMR sometimes allow one to study *faster* chemical exchange processes than ^1H NMR of the same compound? [4]

(c) The magnetogyric ratio of the electron is $\gamma_e = -1.761 \times 10^{11} \text{ T}^{-1}\text{s}^{-1}$.

(i) Discuss the differences between ^1H NMR and EPR (electron paramagnetic resonance) or ESR (electron spin resonance) in the light of the different values of γ_H and γ_e . [8]

You may wish to include some or all of the following in your discussion:

populations of energy levels, sensitivity, spin-spin coupling, spin relaxation, linewidths, spectral resolution, time resolution, applications.

(ii) The 9.25 GHz EPR (ESR) spectrum of the radical $\text{HO}\cdot\text{CH}\text{-COOH}$ in aqueous solution comprises four lines at field positions $3298.160 \pm 0.985 \text{ mT}$, and $3298.160 \pm 0.725 \text{ mT}$. Explain the appearance of this spectrum by means of an energy level diagram. [4]

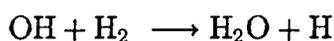
2. Theories of kinetics

(a) The temperature dependence of experimentally derived rate coefficients is often parametrized using the Arrhenius equation.

What are the parameters of the Arrhenius equation, and how can they be determined from experimental data? [4]

(b) Comment on the observation that bimolecular gas phase reactions with small activation energies often show deviations from Arrhenius-type behaviour. [4]

(c) The gas phase reaction



has the following rate coefficients (in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$) for the $v = 0$ and $v = 1$ vibrational states of H_2 :

$$k_{v=0} = 9.3 \times 10^{-12} \exp\left(-\frac{18000}{RT}\right)$$

$$k_{v=1} = 6.0 \times 10^{-11} \exp\left(-\frac{11000}{RT}\right)$$

where RT is in J mol^{-1} .

(i) Calculate $k_{v=0}$ and $k_{v=1}$ at 300, 500, 1000, 1600 and 2500 K and comment on the relative values. [5]

(ii) The $v = 1 \leftarrow v = 0$ excitation energy for H_2 is 49.6 kJ mol^{-1} .

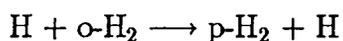
Calculate the fraction of molecules, $f_{v=0}$ and $f_{v=1}$, in each vibrational level at each of the above temperatures. [5]

(iii) Hence calculate the thermal rate coefficient at each temperature using

$$k(T) = k_{v=0}f_{v=0} + k_{v=1}f_{v=1}$$

Present the results as an Arrhenius plot and comment on its shape. [6]

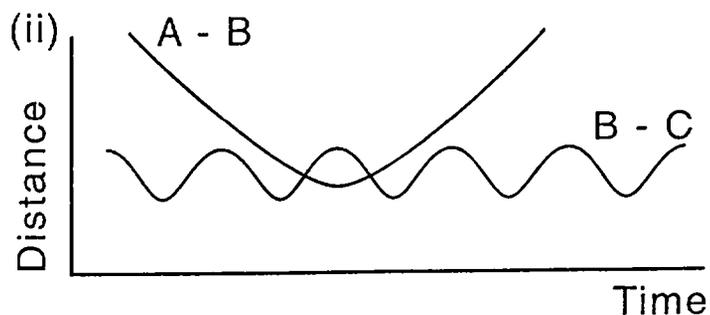
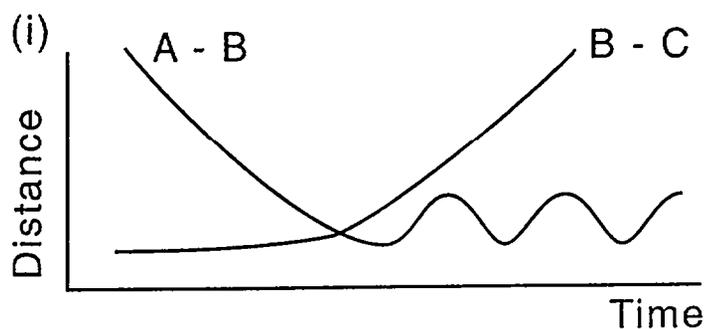
(d) When the Arrhenius expression is used to analyse experimental rate coefficients for the conversion of ortho- into para-hydrogen



the values of the parameters so obtained differ, depending on whether the analysis is performed over the temperature range 290 – 310 K or 390 – 410 K. Discuss possible explanations for this result, and suggest an experiment that could be used to verify the origin of the effect. [5]

(e) The diagrams below show typical classical trajectories for co-linear collisions of an atom A and a diatomic molecule BC in the gas phase.

Comment on this behaviour in the light of the form of the potential energy surface for the A + BC reaction. [5]



3. Molecular interactions: colloids

(a) Discuss the factors affecting the stability of colloidal systems with particular reference to the following observations:

(i) As_2S_3 sols (negatively charged) can be coagulated by a very much smaller concentration of aqueous CaCl_2 than of aqueous KCl .

(ii) The addition of water-soluble polymers often helps to stabilize colloidal dispersions.

(iii) The stability of colloidal sols of many metal oxides in water is sensitive to pH. [12]

(b) For a system where there are no ions present the interaction energy between two parallel slabs is of the form

$$U = -\frac{A}{\tau^m}$$

where τ is the separation and A is a constant. Explain how this relates to the intermolecular potential between two atoms and indicate with justification the likely value of m . [8]

(c) For a vertical liquid film on a solid in equilibrium with vapour and in contact with bulk liquid the thickness τ of the film is related to the height h above the surface by

$$h = \frac{1}{\rho g} \left(\frac{dU}{d\tau} \right)$$

where U is the energy of interaction of uniform slabs of vapour and solid across an intervening liquid medium, ρ is the density of the liquid and $g = 9.8 \text{ m s}^{-2}$. Assuming that the interaction energy follows the equation in (b) show that the thickness of the film varies with height according to

$$\frac{1}{\tau^{m+1}} = Bh$$

where B is a constant. [8]

(d) Measurements of the thickness of a film of helium on a freshly cleaved surface of BaF_2 as a function of height above the surface gave the following results.

h/nm	400	1350	6800	22800
τ/nm	5.2	3.8	2.6	1.9

Interpret the results using the equation in (c) and hence determine the value of m . [6]

4. Reaction dynamics

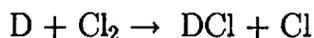
(a) When irradiated with light of wavelength 347.1 nm, Cl₂ dissociates into Cl atoms which are found to be distributed predominantly along directions perpendicular to the electric vector of the incident light, each with a velocity relative to the centre of mass of 3558 m s⁻¹.

(i) Sketch the molecular orbital diagram for Cl₂ and suggest a possible electronic transition that could explain the observations. [4]

(ii) The lowest electronic states of the Cl atom are ²P_{3/2} and ²P_{1/2}, with a separation of 881 cm⁻¹. Which is the lower of the two states? [1]

(iii) Use the data to determine the final state of the Cl atoms. The dissociation energy of Cl₂ is 239.5 kJ mol⁻¹. You may take the mean internal energy of the Cl₂ molecule at the start of the photodissociation to be about 7 kJ mol⁻¹. [You should use the average mass of a chlorine atom, $m_{Cl} = 35.45$ u] [6]

(b) In the molecular beam reaction



DCl is scattered predominantly in the backwards direction. When the initial velocity of D relative to Cl₂ was 6640 m s⁻¹ the most probable velocity of Cl relative to DCl (corresponding to exact backwards scattering) was found to be 3235 m s⁻¹.

(i) Estimate what fraction of the available energy becomes translational energy of the products and give an explanation of the observed distribution of energy. The dissociation energy of DCl is 427.8 kJ mol⁻¹ (use the values of the dissociation energy and mean internal energy of Cl₂ from (a)(iii)). [5]

(ii) What form of potential energy surface is consistent with the observed angular distribution and energy disposal? [2]

(iii) By comparison with the outcome of the photochemical dissociation in (a) suggest the optimum configuration of the reactants for the reaction to occur. [3]

(iv) Account for the observation that, although the angular distribution of DCl peaks along the backwards direction, it has a significant half-width (about 45°). [3]

Question continues

Turn over

(c) The reaction between H atoms and the mixed halogen ICl can give HI and Cl as products or HCl and I. The dissociation energies of ICl, HCl and HI are respectively 207.8, 427.8, and 295.4 kJ mol⁻¹.

(i) Show that the reaction A



is energetically preferred to B

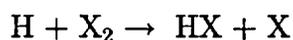
[2]



(ii) In a molecular beam experiment the cross section of the energetically less favoured reaction, B, is a factor of five times greater than that of A. Rationalize this behaviour in terms of the expected relative stability of linear HClI and linear HICl.

[5]

(d) The backwards scattering of HX in the reaction



becomes progressively less pronounced in the series X = Cl, Br, I. Discuss factors that could contribute to this observation.

[3]

5. Answer either Part A or Part B

Part A. Vibrational spectroscopy: group theory

(a) The wavenumbers $\tilde{\nu}$ of the fundamental vibrations of allene C_3H_4 (propadiene) and characteristics of the gas phase Raman and infrared spectra are given in the table below. Show from this information that the vibrations of allene are consistent with the point group D_{2d} . Assign the symmetry species of as many of the vibrations as you can from the information given. The symbols \parallel and \perp indicate that the transition moment is parallel (z) or perpendicular (x, y) to the main symmetry axis. The abbreviations pol., dep. and inact. are abbreviations of polarized, depolarized and inactive. Only totally symmetric vibrations give a polarized signal in the Raman effect. [12]

$\tilde{\nu}/\text{cm}^{-1}$	3085	3005	2996	1957	1440	1398	1076	1015	865	842	354
IR	\perp	\parallel	inact.	\parallel	inact.	\parallel	inact.	\perp	inact.	\perp	\perp
Raman	dep.	dep.	pol.	dep.	pol.	dep.	pol.	dep.	dep.	dep.	dep.

(b) Explain how the spectra would change when two hydrogen atoms at one end of the molecule C_3H_4 are replaced with deuterium. Would this help you to refine your assignment in (a)? [6]

(c) Tetrafluoroallene (C_3F_4) also belongs to the point group D_{2d} . In direct experiments the signals were too weak for all the bands to be observed and some were inactive (all are given the designation abs. in the table). The wavenumbers of the bands observed and the characteristics of the Raman and infrared spectra are given in the table below. One fundamental vibration was not observed in either spectrum.

$\tilde{\nu}/\text{cm}^{-1}$	2050	1249	1040	744	612	580	547	394	159	78
IR	\parallel	\perp	\parallel	abs.	\perp	\parallel	\perp	abs.	not measured	not measured
Raman	abs.	dep.	abs.	pol.	dep.	abs.	dep.	pol.	dep.	dep.

Use the information in the table to identify the symmetry species of the missing fundamental vibration and assign symmetry species to as many of the vibrations as possible. [8]

(d) As well as the fundamental bands listed in (c) further bands in the infrared spectrum of C_3F_4 , all binary combinations of fundamentals, were observed and are listed below. Assign symmetry species to all these combinations and use them to complete your assignment of all the fundamental vibrations. Hence determine the wavenumber, $\tilde{\nu}$, of the missing fundamental vibration. Note that anharmonicity will generally cause the wavenumber of a combination band to be less than the sum of the fundamental wavenumbers. [8]

$\tilde{\nu}/\text{cm}^{-1}$	975	1159	1390	1635	2134	2795	3616
IR band	\parallel	\perp	\perp	\perp	\parallel	\perp	\parallel

Question continues

Turn over

Part B. Quantum mechanics

The wavefunction of an electron in the 2s orbital of a hydrogen atom may be written

$$\psi = N(2 - \rho) \exp\left(-\frac{\rho}{2}\right)$$

where N is a normalisation constant and $\rho (= r/a_0)$ is the distance of the electron from the nucleus, in units of the Bohr radius a_0 .

(a) Sketch the variation of ψ with ρ , locating the positions of any radial nodes. [3]

(b) Sketch the probability of finding the electron at a distance ρ from the nucleus. [3]

(c) Show that the most probable distance is given by $\rho = 5.24$. [10]

You may find the following useful:

$$x^3 - 8x^2 + 16x - 8 = (x - 2)(x^2 - 6x + 4)$$

(d) Calculate the average distance ρ of the electron from the nucleus. [8]

You may find the following useful:

$$\int_0^{\infty} x^n \exp(-ax) dx = \frac{n!}{a^{n+1}}$$

(e) The virial theorem states that for a particle subject to a potential energy of the form $V \propto r^s$, the mean kinetic energy $\langle T \rangle$ and the mean potential energy $\langle V \rangle$ are related by

$$\frac{1}{2}s \langle V \rangle = \langle T \rangle$$

(i) Determine $\langle V \rangle$ and $\langle T \rangle$ for a 2s electron in terms of the Rydberg constant, \mathfrak{R} . [4]

(ii) Determine the classical turning point of the motion of a 2s electron, using [4]

$$\mathfrak{R} = \frac{e^2}{8\pi\epsilon_0 a_0} \text{ and } V = -\frac{e^2}{4\pi\epsilon_0 r}$$

(iii) Comment on the fact that the electron can exist in regions of space where its potential energy exceeds its total energy. [2]

6. Molecular interactions: polymers

(a) When $\kappa R_g \ll 1$ the intensity, I , of x-ray or neutron scattering from a polymer molecule obeys the law

$$I = I_0 \exp\left(-\frac{\kappa^2 R_g^2}{3}\right)$$

where I_0 is the incident intensity, κ is related to the angle of scattering, and R_g is the radius of gyration. The following scattering data were obtained for a sample of poly(styrene) ($M_n = 100,000 \text{ g mol}^{-1}$) dissolved in cyclohexane at 36°C :

$\kappa/(\text{nm})^{-1}$	0.1	0.2	0.3	0.4
$I/\text{arbitrary units}$	0.776	0.365	0.103	0.018

Determine R_g of the polymer. [8]

(b) For two other samples of poly(styrene) in cyclohexane at 36°C of $M_n = 50,000$ and $500,000 \text{ g mol}^{-1}$, R_g was found respectively to be 6.2 nm and 19.5 nm. Comment on these values in relation to each other and to the result from (a). [8]

(c) When carbon disulphide was used as solvent instead of cyclohexane the values of R_g for the three poly(styrene) samples were, in order of increasing M_n , 7.8, 12.7 and 31.0 nm. Comment on the difference in these values from those in cyclohexane and from each other. [7]

(d) The radius of gyration of a polymer can be related to the number of monomer units N in the polymer and the length l of a monomer unit by

$$R_g^2 = \frac{N}{6} sl^2$$

Explain the significance of the term s in this formula.

The radius of gyration of a sample of poly(ethylene oxide) (PEO) of molecular weight $M_n = 22,000 \text{ g mol}^{-1}$ in a θ solvent was found to be 4.8 nm. Comment on the difference between the value for the PEO and the value of 6.2 nm obtained for the $M_n = 50,000 \text{ g mol}^{-1}$ sample of poly(styrene). (A monomer unit of poly(styrene) has a molar mass of 104 g mol^{-1} and a length of 0.26 nm and a monomer unit of poly(ethylene oxide) has a molar mass of 44 g mol^{-1} and a length of 0.36 nm.) [11]

7. Answer either Part A or Part B

Part A. Molecular spectroscopy

(a) (i) Show that the wavenumbers of the Stokes lines in the rotational Raman spectrum of a linear molecule are given by

$$\tilde{\nu}(J) = \tilde{\nu}_i - 2B(2J + 3)$$

where B is the rotational constant, $\tilde{\nu}_i$ is the wavenumber of the incident radiation, and $J = 0, 1, 2, 3, \dots$ [4]

(ii) The rotational Raman spectrum of $^{14}\text{N}_2$ is observed using light of wavenumber 29697.2 cm^{-1} . Stokes lines were observed at the following wavenumbers (in cm^{-1}):

29685.2	29677.3	29669.4	29661.4
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Calculate the value of B for $^{14}\text{N}_2$ and $^{15}\text{N}_2$. [4]

[Atomic masses: $^{14}\text{N} = 14.0 \text{ u}$, $^{15}\text{N} = 15.0 \text{ u}$]

(b) (i) Calculate the moments of inertia of $^{12}\text{C}^{32}\text{S}_2$ and $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ from the following data.

Atomic masses: $^{12}\text{C} = 12.0 \text{ u}$; $^{16}\text{O} = 16.0 \text{ u}$; $^{32}\text{S} = 32.0 \text{ u}$.

Bond lengths: $R(\text{C-S})$ in CS_2 : 154.7 pm

$R(\text{C-S})$ in OCS 157.2 pm

$R(\text{C-O})$ in OCS 112.5 pm

The centre of mass of OCS is 53.8 pm away from the C atom. [6]

(ii) Comment on the observation that the line spacings in the rotational Raman spectrum of CS_2 and OCS are roughly similar. The nuclear spin quantum number of ^{32}S is zero. [5]

(iii) Outline how the bond lengths of OCS may be determined using rotational Raman spectroscopy. [3]

(c) A homonuclear diatomic molecule X_2 has first and second rotational Raman Stokes lines that are shifted from the wavenumber of the incident light by 14.457 cm^{-1} and 26.023 cm^{-1} . Deduce:

(i) the nuclear spin of X, [4]

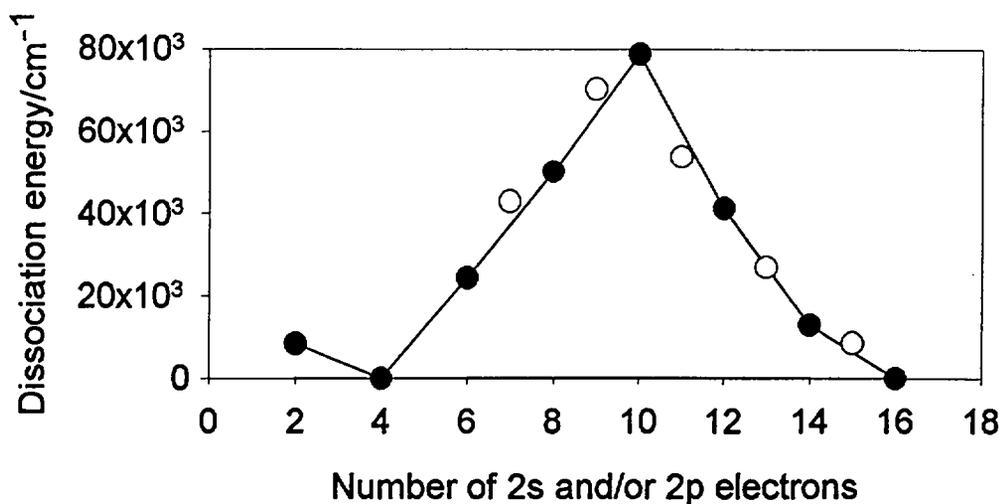
(ii) the symmetry of the electronic state of X_2 , [4]

(iii) the rotational constant of X_2 . [4]

Part B. Valence

(a) Draw the molecular orbital diagram appropriate for the series of homonuclear diatomic molecules from Li_2 to F_2 . Indicate how you would expect the order of orbital energies to change along the series, giving your reasons. [6]

(b) Use your diagram and any other arguments that you need to explain the pattern of dissociation energies of the homonuclear diatomic molecules shown as solid circles in the diagram below and a selection of their positive ions shown as open circles. [4]



(c) Explain the following:

(i) The ground states of B_2 and O_2 are both ${}^3\Sigma_g^-$. [2]

(ii) The ground state of C_2 is ${}^1\Sigma_g^+$ but the energy of this state is only very slightly lower than a ${}^3\Pi_u$ state and there are several other low lying electronic states. [4]

(iii) The first two bands in the photoelectron spectrum of F_2 both exhibit spin-orbit coupling. [3]

(d) Discuss how the pattern of molecular orbitals that you have created in (a) changes for heteronuclear diatomic molecules. [4]

Discuss the following:

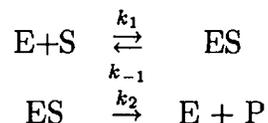
(i) The photoelectron spectrum of CO is similar to that of N_2 . [3]

(ii) NO is paramagnetic and the paramagnetism varies with temperature, whereas the paramagnetism of O_2 is temperature independent. [5]

(iii) The first band in the photoelectron spectrum of HCl is a doublet with an ionization potential and spin-orbit coupling very similar to that of the Cl atom. [3]

8. Enzyme kinetics

An enzyme (E) catalyses the conversion of a substrate (S) into reaction products (P) according to the reaction scheme



(a) Show that under certain conditions

$$\frac{d[P]}{dt} = \frac{k_{cat}[S]}{K_m + [S]}$$

where $k_{cat} = k_2[E]_0$ and $[E]_0$ is the total enzyme concentration. Relate the Michaelis constant, K_m , to the rate constants in the above scheme. Identify and justify any assumption made in your derivation. [8]

(b) The hydrolysis of methylhydrocinnamate (MHC) is catalysed by the enzyme chymotrypsin. The data below relate to 298 K, a pH of 7.6 and a constant enzyme concentration.

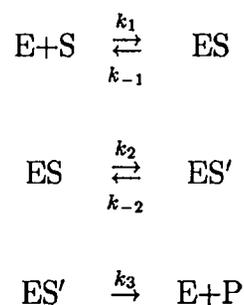
$10^3[\text{MHC}]/\text{M}$	14.6	8.57	4.60	2.24	1.28
$10^8 \text{ Rate}/\text{M s}^{-1}$	17.5	15.0	11.5	7.5	5.0

Evaluate k_{cat} and K_m .

[10]

(c) Ethanol is removed from blood through the action of the enzyme alcohol dehydrogenase. Wary imbibers know that it takes 1-2 hours (depending on the individual) to breakdown the alcohol ingested in every pint of beer drunk. What does the observation of this ethanol-independent rate imply about the kinetic order of the reaction between ethanol and alcohol dehydrogenase? Rationalise this result in terms of your answer to (a) and identify the rate determining step in terms of the above kinetic scheme [6]

(d) It is thought that in some enzyme catalysed reactions more than one intermediate is involved. Consider the scheme



Show that this mechanism also conforms to the rate law given in part (a) and find expressions for k_{cat} and K_m in terms of the rate constants k_1 , k_{-1} , k_2 , k_{-2} and k_3 in the scheme above. What experimental methods might be used to discover if a system showing steady-state kinetics given by the expression in part (a) obeyed the above mechanistic scheme or the simpler version?

[10]

9. Answer either Part A or Part B

Part A. Thermodynamics

A paper published in 1947 described wartime work which determined the vapour pressure, P/Torr , of the compound $(\text{ClCH}_2\text{CH}_2)_2\text{S}$ as a function of temperature, T/K :

$$\log_{10} P = 38.525 - \frac{4500}{T} - 9.86 \log_{10} T$$

The melting point of the compound was found to be 14.4°C .

(a) Starting from the definitions of free energy, G , enthalpy, H , and internal energy, U show that [4]

$$dG = VdP - SdT$$

(b) Use the result in (a) to derive the Clapeyron equation describing phase equilibrium:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

where ΔV is the volume difference between the two phases and ΔH is the enthalpy change associated with the phase transition. [3]

(c) Show that for solid-vapour or liquid-vapour systems: [3]

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$$

Hence determine the enthalpy of vaporization of the compound at 54.0°C and 104.0°C . [2]

(d) Derive Kirchoff's equation:

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$$

where ΔC_P is the difference in the heat capacities of the two phases at constant pressure. [3]

(e) Use the results in (c) and (d) to justify the form of the temperature dependence of the vapour pressure of the compound given above. [6]

(f) Given that the enthalpy of fusion of the compound is 17.6 kJ mol^{-1} estimate the vapour pressure above the compound at the melting point and at 10°C . [4]

(g) The concentration of the compound during an experiment was determined by passing the gas through aqueous acid leading to its rapid hydrolysis (loss of Cl^-). This was carried out in a titration vessel with a silver wire electrode and the “quantity of chloride was determined potentiometrically using 0.2 M AgNO_3 ”. Explain the likely basis of this procedure. [3]

(h) Prior to experimentation the liquid compound was purified via distillation using a fractionating column. Explain the basis of this procedure. [3]

(i) Further purification was done by fractional freezing: the liquid compound was placed in a glass jar surrounded by crushed ice and the solid scraped off the sides of the jar as fast as it was formed. Explain the basis of this procedure. [3]

Part B. Statistical mechanics

(a) The energy levels of a particle of mass m confined in a one-dimensional box of length l are given by

$$\varepsilon_n = \frac{n^2 h^2}{8ml^2}$$

(i) Define q , the molecular partition function for the translational motion of the particle. [2]

(ii) Prove that

$$q = \frac{V}{\Lambda^3}$$

where

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

for a particle of mass m moving in a three-dimensional box of volume V , at temperature T , justifying any approximations made. [6]

Note that

$$\int_0^\infty \exp(-\alpha^2 u^2) du = \frac{\sqrt{\pi}}{2\alpha}$$

(iii) The Boltzmann distribution is applicable to a system of non-interacting, indistinguishable molecules (or atoms) if the number of quantum states thermally accessible to a molecule greatly exceeds the number of molecules in the system. Show that this is equivalent to the condition that the thermal wavelength Λ is much smaller than the mean intermolecular separation, r_0 . [Note that the number of thermally accessible quantum states is approximately equal to the molecular partition function of the system.] [4]

(iv) Consider 5×10^{22} atoms of helium gas contained in a volume of 1 cm^3 . At what temperature does Λ become equal to r_0 ? What are the implications of your result? [$m_{He} = 4 \text{ u.}$] [4]

(b) The internal energy of a system of N non-interacting particles in a volume V at temperature T is given by

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

(i) Calculate the molar internal energy of a gas of non-interacting atoms. [5]

(ii) The entropy of the system is given by

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

Using $dA = -pdV - SdT$, prove that [3]

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

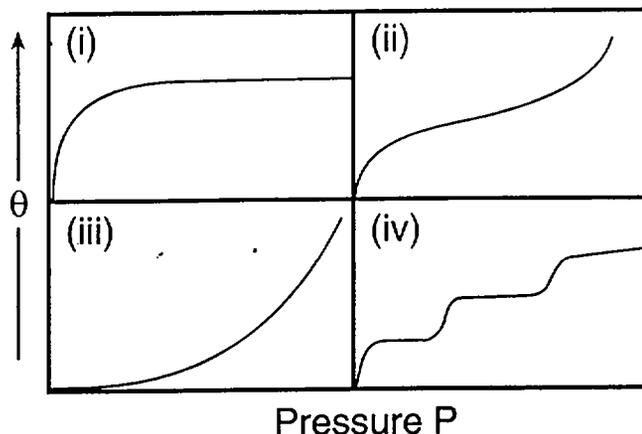
(iii) Hence obtain an equation of state for non-interacting atoms in the gas phase. [3]

(iv) Obtain an expression for C_p , the constant pressure heat capacity and compare it with the predictions of classical mechanics. [3]

(v) Give a physical explanation of the dependence of S on m , T and V . [4]

10. Surfaces

(a) The adsorption isotherms shown below relate to (i) 'Langmuir' behaviour, (ii) BET-type adsorption, (iii) H₂O adsorption on polyethylene, and (iv) noble gas adsorption on well-defined, uniform solids such as highly oriented pyrolytic graphite. Explain qualitatively the observed behaviour in each case. [8]



(b) Describe the techniques of scanning tunnelling and atomic force microscopies and explain how they provide information about solid surfaces.

A simple model predicts the STM tunnelling current (I) to depend exponentially on the sample to tip gap (S)

$$I \propto \exp[-2kS]$$

The following data were recorded in an STM experiment for a fixed bias voltage

$S/\text{\AA}$	4.5	5.0	5.5	6.0	6.5
I/nA	13.6	4.99	1.84	0.68	0.25

Show that the data are consistent with the model and evaluate the constant, k . Suggest a basis for the model. [12]

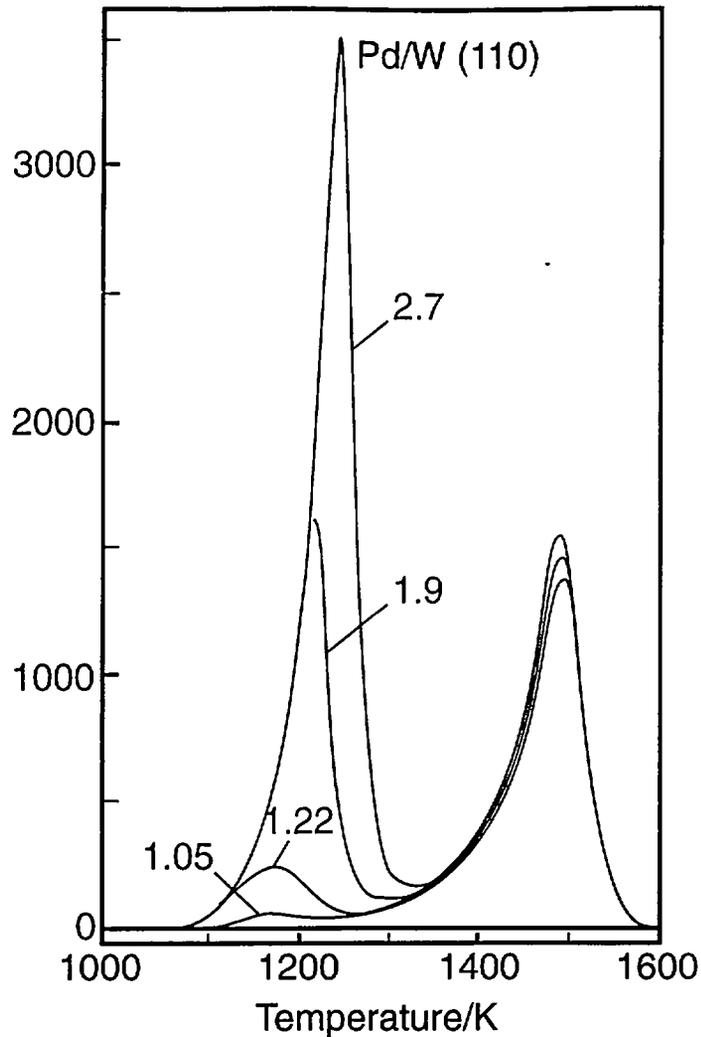
(c) (i) Explain how the technique of temperature programmed desorption (TPD) can give information about adsorption on solid surfaces.

(ii) The figure on the next page shows thermal desorption spectra for palladium on W(110) as a function of coverage up to a maximum of 2.7 monolayers.

Comment qualitatively on the changes in area under the peaks in the figure.

Question continues

Turn over



(iii) The rate of the desorption process may be formulated as

$$-\frac{dN}{dt} = A(e^{-E_d/RT})N^m$$

where N is the number of adsorbed molecules, A is a constant and m is the order of the reaction.

Explain the physical significance of the exponential term and show that if a linear temperature programme,

$$T = T_0 + \beta t$$

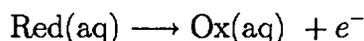
is applied then at the temperature, T_P , of the thermal desorption peak maximum (where $\frac{d^2N}{dT^2} = 0$)

$$\frac{E_d}{RT_P^2} = \frac{A}{\beta} m N^{m-1} e^{-E_d/RT_P}$$

Hence show that for first order desorption kinetics the desorption peak maximum is independent of N but that for second order processes T_P decreases as N increases assuming E_d is constant. [14]

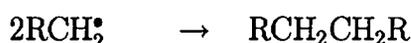
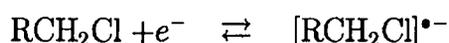
11. Dynamic electrochemistry

(a) (i) Describe and explain the current-voltage curve seen for the oxidation reaction



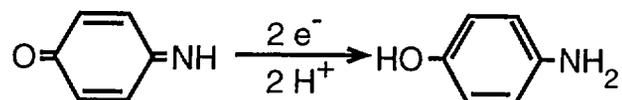
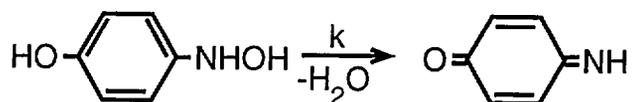
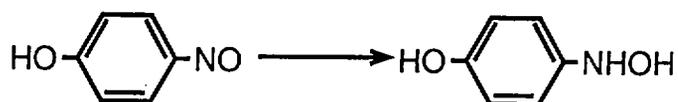
when both Ox and Red are stable, and when Ox is unstable (relative to the speed of the voltage scan). [8]

(ii) The electroreduction of 2-nitrobenzylchloride ($2\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}_2\text{Cl}$) in liquid ammonia is thought to proceed via the following mechanism.



How would you use cyclic voltammetry to verify this mechanism? [4]

(iii) The reduction of 4-nitrosophenol in aqueous ethanol is thought to proceed via the following mechanism.



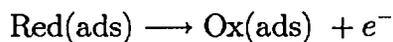
with the formation of 4-aminophenol. What cyclic voltammetry experiments would you perform to verify this mechanism and to determine the rate constant, k ? [6]

(iv) The $\text{MnO}_4^{2-}/\text{MnO}_4^-$ redox couple shows fast electrode kinetics, the $\text{Fe}(\text{H}_2\text{O})_6^{2+}/\text{Fe}(\text{H}_2\text{O})_6^{3+}$ couple is more sluggish and the $\text{Eu}^{2+}/\text{Eu}^{3+}$ couple is very slow. Explain how these differences could be revealed by cyclic voltammetric measurements. [4]

Question continues

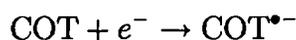
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(v) Cyclic voltammograms for the oxidation of adsorbed species,

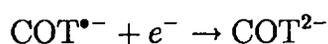


show a different shape from those seen for solution phase species. Comment. [2]

(b) In non-aqueous solvents cyclo-octatetraene (COT) undergoes reduction to the mono anion and the dianion in two separate voltammetric steps. The rate constant for



is approximately two orders of magnitude lower than for



Comment in the light of Marcus theory. [5]

(c) The figure below shows the relative rate of hydrogen evolution from aqueous acid solution for various electrode materials as a function of the estimated metal-hydrogen bond strength. Comment and explain why you would expect a transfer coefficient of $\frac{1}{2}$ for the electrode reaction on some of the metals shown but a value of $\frac{3}{2}$ for the others. [5]

