

## HONOUR SCHOOL OF NATURAL SCIENCE

## Final Examination

## ADVANCED PHYSICAL CHEMISTRY

Tuesday, 10th June 1997, 2.30 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.

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Speed of light, $c$	=	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck's constant, $h$	=	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann's constant, $k_B$	=	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Molar gas constant, $R$	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro's number, $N_A$	=	$6.022 \times 10^{23}$
1M	=	$1 \text{ mol dm}^{-3}$
$p^\ominus$	=	$1 \text{ bar} = 10^5 \text{ Pa} \simeq 1 \text{ atm}$
$V_m^\ominus$	=	$24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K
Elementary charge, $e$	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, $u$	=	$1.661 \times 10^{-27} \text{ kg}$

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Turn over

1. The table below lists the electrostatic, induction and dispersion contributions to the intermolecular attractive potential energy for water and ammonia, calculated in each case for an intermolecular separation of 0.3 nm.

	$U_{el}$	$U_{ind}$	$U_{disp}$	/kJ mol <sup>-1</sup>
NH <sub>3</sub>	-6.2	-0.9	-12.9	
H <sub>2</sub> O	-16.1	-0.9	-5.3	

(a) Use these data to estimate (i) the ratio of the dipole moments and (ii) the ratio of the polarizabilities for ammonia and water. Give an explanation for which molecule has the larger polarizability. [6]

[The ionization potentials of ammonia and water are 10.4 and 12.6 eV, respectively]

(b) The quantities given in the table are calculated for 300 K; discuss how these quantities will change with increase in temperature to 350 K and explain the physical basis of any temperature dependence predicted. [5]

(c) How would the quantities change if calculated for a distance of 0.35 nm? [2]

(d) Discuss the physical origin of short range repulsive forces. [4]

(e) Explain what is meant by the pair distribution function for a liquid, and sketch the atom-atom distribution functions  $g_{(O-O)}$  and  $g_{(O-H)}$  for H<sub>2</sub>O. [5]

(f) The interaction energy per unit area between two sheets of quartz separated by a layer of water, thickness  $D$ , is given by

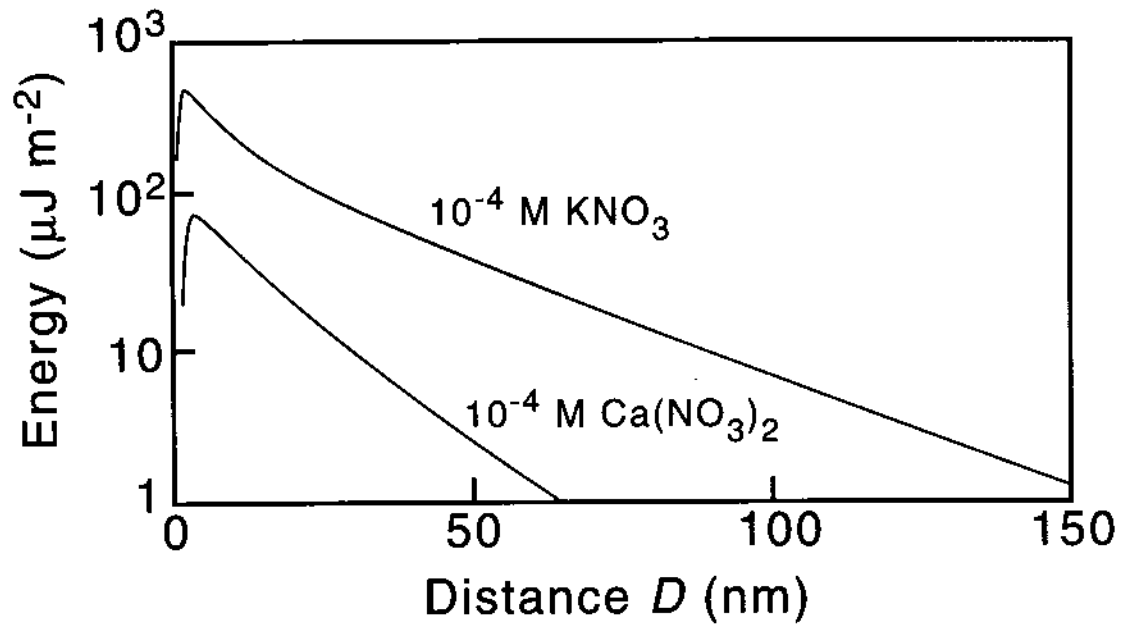
$$E = -A_{131}/12\pi D^2.$$

where  $A_{131}$  is a Hamaker constant.

(i) Show that  $A_{131} = A_{11} + A_{33} - 2A_{13} \simeq A_{11} + A_{33} - 2\sqrt{(A_{11}A_{33})}$

(ii) Hence, using the values,  $A_{11} = 11.0 \times 10^{-20}$  J for quartz and  $A_{33} = 5.8 \times 10^{-20}$  J for water, calculate the force between two quartz sheets of area 1 cm<sup>2</sup>, separated by 2 nm. [6]

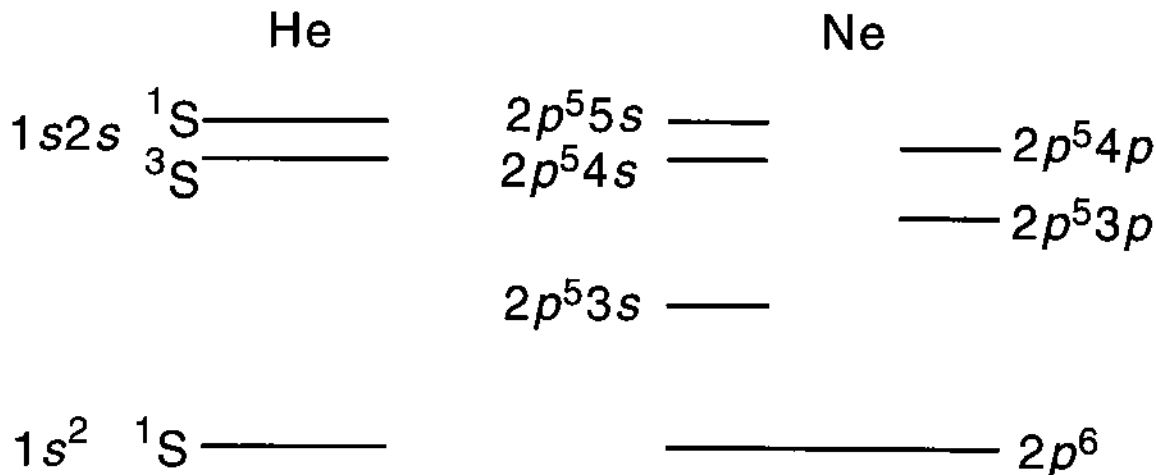
(g) The energy of interaction between two charged mica sheets measured with a surface force apparatus in  $10^{-4}\text{M KNO}_3$  and  $10^{-4}\text{M Ca(NO}_3)_2$  appears as shown in the following figure. Comment on the trends shown. [5]



2. ANSWER BOTH PARTS A AND B

A.

The following diagram shows some of the electronic energy levels for gaseous helium and neon atoms.



Describe the mechanism by which a population inversion can be created in this medium and explain how this inversion is exploited in the operation of the helium-neon laser. [10]

B.

(i) The term symbols arising from the lowest energy configuration of the titanium atom ( $3d^24s^2$ ) are  $^1G$ ,  $^3F$ ,  $^1D$ ,  $^3P$  and  $^1S$ . Using Hund's Rules explain which of these terms is the ground state. [3]

(ii) Explain why the  $^3G$  term does not exist for this configuration. [3]

(iii) Write (i) a spin wavefunction for the two 3d electrons in the  $^1G$  term of the  $3d^24s^2$  configuration of Ti, and (ii) an orbital wavefunction for the two 3d electrons in the  $M_L=3$  component of the  $^1G$  term so as to obey the Pauli Principle.

Show that the expectation value of the electron-electron repulsion operator for the orbital wavefunction may be written in the form  $\mathcal{J} + \mathcal{K}$ , where  $\mathcal{J}$  and  $\mathcal{K}$  are Coulomb and Exchange integrals respectively. [7]

(iv) Show that for an atom obeying Russell-Saunders coupling, the expectation value of the spin-orbit operator  $H_{SO}=AL.S$  is

$$\langle H_{SO} \rangle = \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)] \hbar^2$$

where  $J$  is the quantum number for the total angular momentum. [4]

(v) In wavenumber units, the preceding equation may be written in the form

$$\langle H_{SO} \rangle / hc = \frac{1}{2} \tilde{A} [J(J+1) - L(L+1) - S(S+1)]$$

(with  $\tilde{A} = A\hbar/2\pi c$ ).

The energy levels (in  $\text{cm}^{-1}$ ) for one of the quintet terms of the titanium  $3d^34s$  configuration relative to the ground state are

6556.86

6598.83

6661.00

6742.79

6843.00

Use a graphical procedure to deduce the spin-orbit coupling constant  $\tilde{A}$  for this term, and identify the  $L$  quantum number. [6]

### 3. ANSWER ALL PARTS

A. The nuclear spin energy levels of a set of weakly coupled nuclei showing a first-order NMR spectrum may be written in the form

$$E/h = \sum_{i < j} J_{ij} m_i m_j - \sum_i \nu_i m_i$$

where  $\nu_i$  is the Larmor frequency for nucleus  $i$ , (i.e., the frequency of the transition for nucleus  $i$  in the absence of spin-spin coupling) and  $J_{ij}$  is the nuclear spin-spin coupling constant. In vinyl acetate  $\text{CH}_2=\text{CHOCOCH}_3$ , the three vinyl protons behave in a 100 MHz NMR spectrum as a weakly coupled AMX system, with spin-spin coupling constants

$$J_{AM} = 1.4 \text{ Hz}$$

$$J_{AX} = 13.8 \text{ Hz}$$

$$J_{MX} = 6.4 \text{ Hz}$$

and chemical shifts

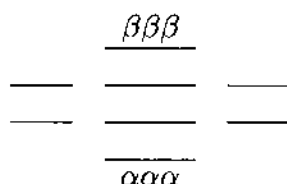
$$\delta_A = 4.85$$

$$\delta_M = 4.55$$

$$\delta_X = 7.25$$

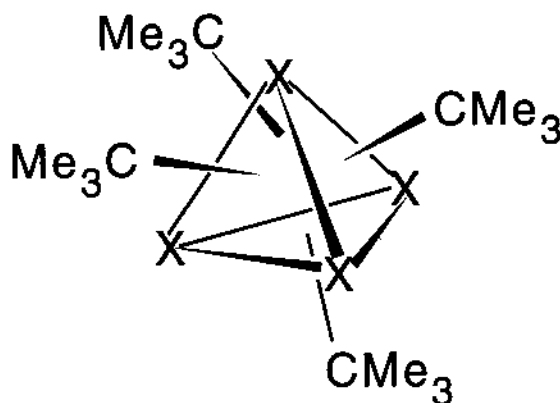
(i) Sketch the overall NMR spectrum of vinyl acetate, showing the relative intensities of the lines, and indicating the magnitude of the spin splittings. [4]

(ii) The diagram below illustrates the energy levels of the three spin system. Complete the labelling of the states with the notation  $\alpha\alpha\alpha$ ,  $\alpha\beta\alpha$  etc. (representing nuclei in the order A,M,X) and indicate which are the allowed NMR transitions between these levels. [3]

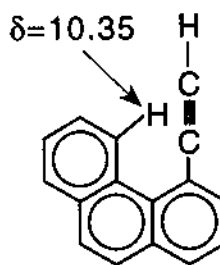
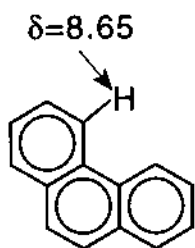


(iii) Calculate the frequencies of the transitions corresponding to the X resonance, assuming that  $\delta = 0$  corresponds to a frequency of 100.000000 MHz, and indicate which pair of energy levels is involved for each transition. [7]

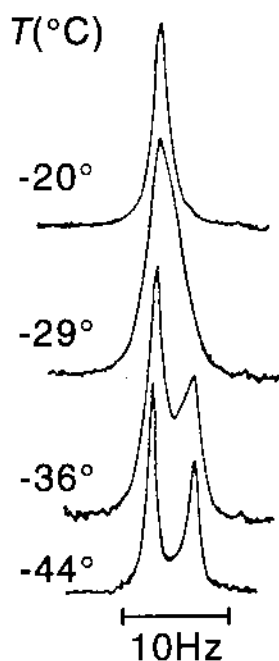
B. The  $^{13}\text{C}$  NMR spectrum of the tetrahedral compound  $\text{X}_4(^{13}\text{CMe}_3)_4$ , for which the structure is shown below, displays a septet with relative intensities 1:3:6:7:6:3:1. Explain the number of the lines and their relative intensities. Suggest a reason why spin-spin coupling patterns associated with nucleus X, or with other nuclei with the same spin quantum number, are often not observed in solution-phase NMR spectra. [6]



C. Explain the difference in the observed chemical shifts for the two compounds indicated below. [6]



D. The figure below shows the 60 MHz proton NMR spectra of 2,2,3,3-tetrachlorobutane over a wide range of temperatures. Explain the changes in the spectrum observed and *estimate* the free energy of activation for the process underlying these changes at a temperature of  $\sim -30^\circ\text{C}$ . What would be the effect on this set of spectra of increasing the spectrometer operating frequency to 100 MHz? [7]





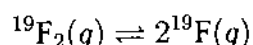
4.  $F_2(g)$  has a rotational constant  $B_0$  of  $0.88 \text{ cm}^{-1}$ , a force constant  $k$  equal to  $445 \text{ Nm}^{-1}$  and a dissociation energy  $D_0$  of  $154.4 \text{ kJmol}^{-1}$ . The energy separation between the  $^2P_{1/2}$  and  $^2P_{3/2}$  levels of  $F(g)$  is  $403 \text{ cm}^{-1}$ .

Consider 1 mole of species at a pressure  $p^\circ$  and a temperature of 1200 K. Under these conditions:

(a) Calculate the translational and electronic contributions to the molecular partition function of  $F(g)$ . [7]

(b) Calculate the translational, rotational and vibrational contributions to the molecular partition function of  $F_2(g)$ . [7]

Hence calculate the equilibrium constant  $K_p$  for the reaction



at a temperature of 1200 K. [8]

What factors might contribute to discrepancies between the observed fraction of fluorine molecules dissociated at 1200 K and a pressure of 1 bar, and the value calculated from your expression for  $K_p$ ? [3]

Describe in detail how the heat capacity,  $C_v$ , of equilibrium mixtures of atomic and molecular fluorine could be calculated by statistical mechanics as a function of temperature from 300 K to a limit where the degree of dissociation,  $\alpha$ , is high. [5]

Discuss what factors contribute to the value of  $C_v$  at this high-temperature limit. [3]

[ $hc/k_B = 1.439 \text{ cm K}$ ; relative atomic mass of  $^{19}F = 19$ ]

5. (a) Show how the Gibbs-Duhem equation,

$$\sum n_i d\mu_i = 0$$

which relates changes in chemical potential of the species present in solution at constant temperature and pressure, may be derived. [5]

The activity coefficients of a solvent A and an involatile solute B in a binary non-electrolyte solution may be defined by the equations,

$$\begin{aligned} \mu_A &= \mu_A^* + RT \ln \gamma_A x_A & \gamma_A &\rightarrow 1 \text{ as } x_A \rightarrow 1 \\ \mu_B &= \mu_B^\dagger + RT \ln \gamma_B x_B & \gamma_B &\rightarrow 1 \text{ as } x_B \rightarrow 0 \end{aligned}$$

where  $x$  denotes mole fraction.

Why must limits be given where  $\gamma$  takes on a prescribed value, and why is it often convenient for the limits for the concentration where  $\gamma$  approaches unity to be different for the solvent and solute? [2]

(b) Describe how vapour pressure measurements and determination of colligative properties can be used to determine the activity coefficient of the solvent,  $\gamma_A$ , as a fraction of solvent mole fraction. [5]

The vapour pressure  $p_A$  of A is found to vary with mole fraction  $x_A$  as B is added to the solution as follows

$p_A/10^4\text{Pa}$	1.200	1.132	1.048	0.751
$x_A$	1.00	0.95	0.90	0.80

Calculate  $\gamma_A$  for the different values of  $x_A$  and show that the data can be expressed approximately at low concentration in the form

$$\ln \gamma_A = \beta x_B^2$$

Calculate the value of  $\beta$ . [7]

(c) By considering changes in chemical potential at constant temperature and pressure with variations in composition  $dx_A$ , show that

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$$

[5]

(d) Hence show that the activity coefficient of species B,  $\gamma'_B$ , at mole fraction  $x'_B$ , is given by the equation

$$\ln \gamma'_B = - \int_0^{\ln \gamma'_A} \frac{1 - x_B}{x_B} d \ln \gamma_A$$

where  $\gamma'_A$  is the activity coefficient of species A in this solution at composition  $x'_B$ . [2]

By considering the limiting form for  $\ln \gamma_A$  at low concentration of B given in (b), show that in these circumstances

$$\ln \gamma_B = \beta(x_A^2 - 1)$$

and calculate the value of  $\gamma_B$  when  $x_A = 0.9$ . [5]

How would you calculate  $\gamma_B$  at higher concentrations of B? [2]

6. (a) Why, in the LCAO approach to MO theory, is it convenient to take the basis set of atomic functions in a form such that they transform like irreducible representations (IRs) of the group appropriate to the molecule concerned? [5]

(b) Explain why the point symmetry group for ammonia is  $C_{3v}$  and deduce the IRs contained in the representation based on the hydrogen 1s orbitals along with one form of the symmetry adapted combinations for each IR. [7]

Hence draw the molecular orbital diagram for the molecule, given that the highest occupied molecular orbital is non-degenerate. [3]

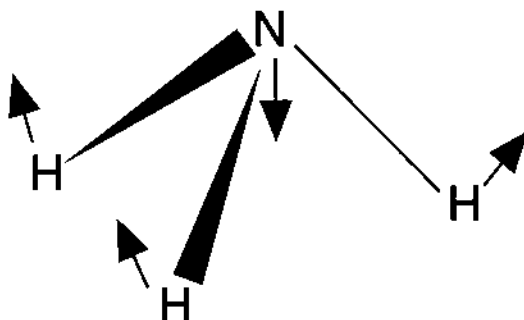
(c) What differences would you expect between the MO diagrams of ammonia and boron trihydride ( $BH_3$ ), when distorted to the same pyramidal geometry? [3]

(d) Assuming  $BH_3$  and  $NH_3$  retain a pyramidal geometry upon formation of the electronic donor-acceptor complex,  $BH_3NH_3$ , suggest the MO diagram for this species. [3]

How is the transfer of electron density from nitrogen to boron represented in this diagram? [2]

(e) Explain how the valence electronic structure of ammonia can be described using a localised bonding model. Comment on the observation that the photoelectron spectrum of the valence electrons in ammonia exhibits three bands. [5]

(f) The PES band associated with ionisation from the highest energy occupied MO in ammonia shows a pronounced vibrational fine structure, with clearly resolved peaks separated by  $900\text{ cm}^{-1}$ . Rationalise why this is so, given that the vibrational frequency of the 'umbrella' mode shown below in neutral ammonia lies at  $950\text{ cm}^{-1}$ . [5]



2713 DCHA

## 7. ANSWER EITHER PART I or PART II

### I Answer both parts A and B

A. Why are low energy electrons used in techniques to investigate solid surfaces and why are such studies limited to low pressures? [3]

Explain the following:

(i) If a beam of electrons is incident normally on a Ni(100) surface, some electrons are back-scattered from the surface in four directions, each lying at an angle  $\theta$  to the surface normal, defined by the equation

$$\sin \theta = h/(2meVd^2)^{\frac{1}{2}}$$

where  $V$  = electron accelerating voltage  $d$ =lattice parameter of the Ni(100) surface, and  $m$  and  $e$  denote the mass and charge of the electron, respectively. [4]

(ii) The kinetic energy of X-ray excited photoelectrons emitted from a surface depends on the X-ray wavelength used. This dependence does not occur for the Auger electrons also emitted during X-ray irradiation. [2]

(iii) Gold is gradually deposited on an aluminium oxide surface, and during the deposition, X-ray excited electron emission spectra are measured as a function of time using 1487 eV X-rays. The oxygen Auger peak rapidly disappears from the spectrum; the O 1s photoelectron peak persists to longer time-scales. (The O 1s level has a binding energy of 530 eV). [4]

(iv) Electrons inelastically scattered from CO(g) may undergo an energy loss of  $\sim 268$  meV. When CO is adsorbed on a surface, this loss peak either occurs at lower energies (220-260 meV) or is not observed. [4]

[1 meV=8.067  $\text{cm}^{-1}$ ]

B. CO at a pressure  $p$  is incident on an initially clean Fe(100) surface which has a lattice parameter of 0.29 nm. The sticking probability of the gas at the surface ( $S_\theta$ ) is found to vary as  $(1-\theta)$ , where  $\theta$  represents the fraction of surface adsorption sites occupied by an adsorbate. For a temperature of 300 K and a pressure  $p = 10^{-5} \text{ Nm}^{-2}$ , LEED indicates that a  $(2 \times 2)$  surface structure forms after 20 s exposure of the surface to the gas. XPS measurements show that the surface lifetime of adsorbed carbon monoxide is long at 300 K. In contrast, CO rapidly desorbs from the surface above 450 K and the following data were measured at two temperatures

time/s	0	5	10	15	20
$\theta(450 \text{ K})$	1	0.56	0.31	0.17	0.10
$\theta(460 \text{ K})$	1	0.31	0.094	0.029	<0.01

2713 DCHA

Question continues  
Turn over

(i) Give an explanation for the coverage dependence of the sticking probability,  $S_\theta$ , and show that  $\theta$  should vary with  $t$ , the exposure time of the surface to the gas, according to

$$\theta = 1 - e^{-At}$$

where

$$A = \frac{pS_0}{(2\pi mk_B T)^{\frac{1}{2}} n}$$

$n$  = number of surface sites  $m^{-2}$   
 $S_0$  = sticking probability at  $\theta = 0$   
 $m$  = molecular mass of CO  
 $T$  = temperature (300 K)

(ii) Explain why the (2 x 2) structure is likely to have a coverage  $\theta = 0.25$ . Estimate  $S_0$ . [6]

(iii) Show that the desorption kinetics are first order with respect to the coverage of adsorbed CO. What does this suggest concerning the nature of the adsorbed layer? [5]

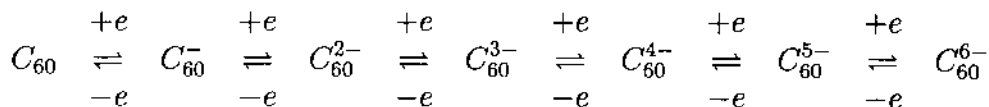
Estimate the heat of adsorption of CO(g) on Fe(100). [5]

[Relative molecular mass of CO = 28 ]

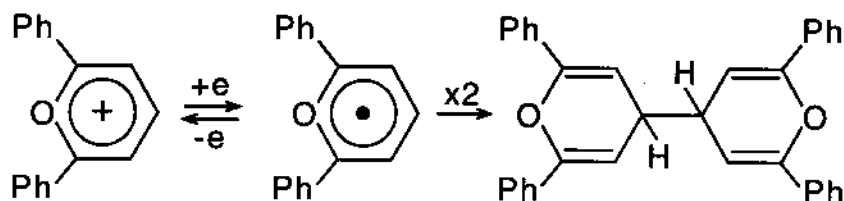
**II Answer part A, and either part B, or part C.**

A. Write an account of *cyclic voltammetry*. Discuss how such measurements may be used to obtain information about electrode reaction mechanisms. Illustrate your answer by explaining how cyclic voltammetry would reveal four of the following.

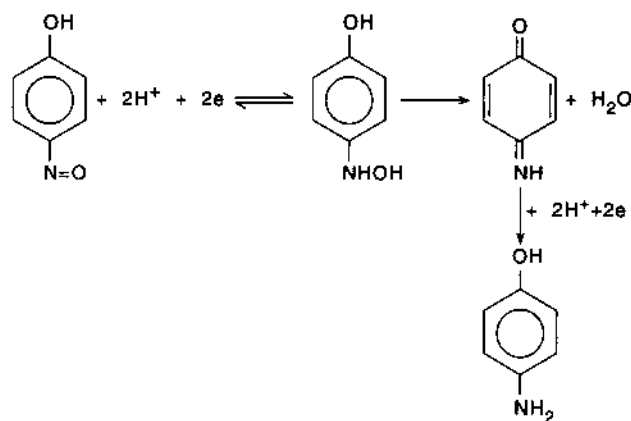
(i)  $C_{60}$  in non-aqueous solvents can undergo up to six separate one electron reductions at platinum electrodes:



(ii) The reduction of the 2,6-diphenyl pyrylium cation in acetonitrile at platinum electrodes produces a radical which undergoes irreversible dimerisation



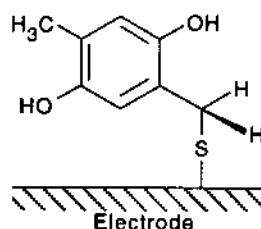
(iii) The reduction of p-nitrosophenol in water at platinum electrodes occurs via the following mechanism



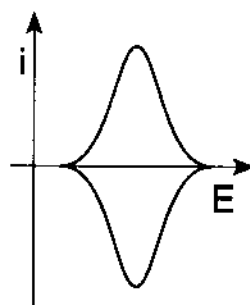
(iv) The kinetics for the reduction of  $\text{Eu}^{3+}$  are significantly slower than for the reduction of  $\text{Fe}^{3+}$  at many electrodes.

(v) Mechanisms of hydrogen evolution at different electrode surfaces. [25]

B. The molecule 2,5-dihydroxy-4-methylbenzylthiol undergoes irreversible adsorption on platinum electrodes to form the species illustrated:

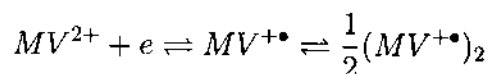


The cyclic voltammogram of the adsorbate is shown below.



Explain why this shows that the adsorbate is anchored to the surface *throughout* the experiment. How might voltammograms such as that in the preceding figure be used to measure adsorption isotherms for electroactive adsorbates? [8]

C. The methyl viologen dication,  $MV^{2+}$ , is thought to undergo electro-reduction in water with the formation of the radical cation,  $MV^{+\bullet}$ , which undergoes *reversible* dimerisation:



How might the cyclic voltammetry differ from that expected for *irreversible* dimerisation? Note that the dimer is NOT electroactive. [8]



## 8. ANSWER BOTH PARTS A AND B

A. Describe how you could analyse:-

(i) the Raman spectrum of  $^1\text{H}_2$ , excited by an  $\text{Ar}^+$  ion laser, to estimate the equilibrium bond length,  $r_e$ , in  $\text{H}_2$ . [6]

(ii) the Raman spectra of  $\text{CO}_2$  and  $\text{O}_2$ , to establish the differing symmetries of their ground electronic states. [6]

(iii) the photoelectron spectrum of  $\text{H}_2$ , excited by a  $\text{He(I)}$  resonance lamp, to estimate the bond dissociation energies  $D_0$  and  $D_e$ , in  $\text{H}_2^+$ , and the vertical ionisation energy of  $\text{H}_2$ . [6]

(iv) the infrared vibration-rotation band spectrum of  $\text{CH}_3\text{F}$ , associated with excitation of (1) its  $\text{CH}_3$  rocking mode,  $\nu_6(E \leftarrow A_1)$  and (2) its symmetric stretching mode,  $\nu_1(A_1 \leftarrow A_1)$ , to estimate its rotational constants, A and B, assuming their magnitudes are the same in both the lower and upper states of the transitions. [6]

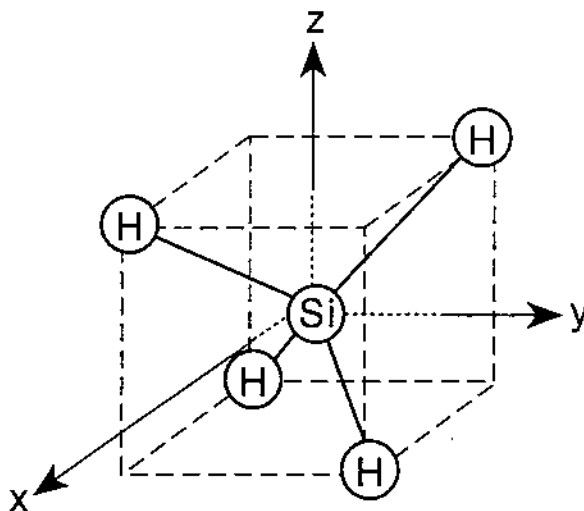
[The molecule  $\text{CH}_3\text{F}$  is a prolate symmetric top, of point group symmetry  $C_{3v}$ ; the selection rules for  $\Delta K$  are,

$\Delta K = 0$  (transitions parallel to the a-inertial axis)

$\Delta K = \pm 1$  (transitions polarised perpendicular to the a-inertial axis)]

B. Explain why a tetrahedral, spherical top molecule, such as  $\text{SiH}_4$ , is not expected to display a pure rotational spectrum. [1]

Because of centrifugal distortion,  $\text{SiH}_4$  actually displays a series of very weak, pure rotational transitions at ca.  $100 \text{ cm}^{-1}$ , with an average spacing of  $5.79 \text{ cm}^{-1}$ . Assuming the rotational term values are still given by  $F(J) = B J(J+1)$ , estimate its rotational constant, B, its moment of inertia I, and its average bond length, R. (The inertial axes are shown as x, y and z, in the following figure). [8]



2713 DCHA

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## 9. ANSWER BOTH PARTS A AND B

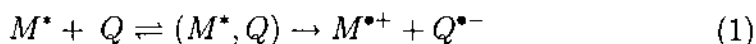
A. What is the basis of the Franck-Condon Principle? [3]

Discuss the importance of the principle in controlling the probabilities of

- (i) radiative, and
- (ii) non-radiative

molecular electronic transitions. What other factors determine the probability of electronic, non-radiative decay processes in isolated polyatomic molecules? [13]

B. According to the Marcus theory, the second order rate constant,  $k_Q$ , for quenching an electronically excited molecule,  $M^*$ , through electron transfer to a quencher molecule,  $Q$ , via the sequence



can be approximated by the expression

$$k_Q \sim V^2 K_{M^*Q} \exp[-(\Delta G^\circ + \lambda^2)/4\lambda RT] \quad (2)$$

where  $\Delta G^\circ$  is the standard free energy change associated with the electron transfer process.

Give a qualitative outline of the theory that leads to this expression and explain the significance of the terms  $V$ ,  $K_{M^*Q}$  and  $\lambda$ . Under what circumstances would the quenching rate, in solution, approach the diffusion controlled limit? How might the ionic product,  $Q^{\bullet-}$ , be detected? [14]

Discuss the significance of the Marcus theory in providing a rationale for the high quantum efficiency of electron transfer in the primary process of photosynthesis. [3]

10. (a) What is meant by the *activation energy*; the *threshold energy*; the *potential energy surface*; the *minimum energy path*; and the *transition state* for a bimolecular reaction? [7]

(b) Discuss the transition-state theory, and its assumptions, successes and limitations. [8]

(c) Show how the so-called thermodynamic formulation leads to the expression

$$A = \frac{k_B T}{h} \left( \frac{RT}{p^\ominus} \right) e^2 \exp(\Delta S^\ddagger / R) \quad (1)$$

for the pre-exponential factor in the Arrhenius equation for the rate constant,  $k(T)$ , of a bimolecular reaction in the gas phase. How may equation (1) be interpreted to imply structural constraints on the transition state for the cyclo-addition of ethene to 1,3-butadiene, given that the pre-exponential factor is  $3.64 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 300 K? [8]

How may direct information on the structures of molecular systems in the region of the transition state be gained? [2]

(d) Comparing both the columns and rows in the table below, discuss the relative magnitudes of the following set of rate constants,  $k$ , all measured at 400 K,

	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
(i) $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$	$2.0 \times 10^6$	(ii) $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$	$3.6 \times 10^6$
(iii) $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$	$0.5 \times 10^6$	(iv) $\text{D} + \text{D}_2 \rightarrow \text{D}_2 + \text{D}$	$0.9 \times 10^6$

The activation energy for reaction (i), determined from the Arrhenius equation at 400 K, is  $33 \text{ kJ mol}^{-1}$ ; at 290 K its rate constant,  $k = 1.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Comment on these two results and their possible interpretation. [8]