

DCHA 2706

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Friday, 6th June 2003, 2.30 p.m. to 5.30 p.m.

Answer *FIVE* out of nine questions

Please begin your answer to each question on a new page

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

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

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

DCHA 2706

Turn over

Fundamental Constants

Speed of light	c	$2.997 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	k_B	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	F	$9.649 \times 10^4 \text{ C mol}^{-1}$
Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	m_p	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	ϵ_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	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$

Other conventions

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

1. Atomic Spectra

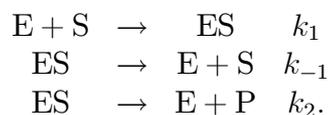
- (a) Explain how the phenomena of *shielding* and *penetration* determine the binding energies of *ns*, *np* and *nd* electrons in the sodium atom, relative to the corresponding levels in hydrogen. [6]
- (b) Account for the fact that some, but not all, of the series in the emission spectrum of Na occur in pairs with a common lower term. [4]
- (c) The transitions with the lowest wavenumbers in two such series are given in low resolution below. Account for the observation that the lines in series I have a fine structure splitting equal to that of the lowest frequency line in the absorption spectrum, which is centered at $16\,968\text{ cm}^{-1}$. How is the fine structure of the lines in series II expected to differ from that in series I? [5]

series I	series II
ν/cm^{-1}	ν/cm^{-1}
8772	12205
16233	17581
19405	20069
21044	21420

- (d) Estimate the limit of series II and hence the ionization energy of Na. [5]

2. Enzyme Kinetics

- (a) The standard enzyme catalysis mechanism is as follows:



Show that the steady state concentration of the enzyme-substrate complex is given by

$$[\text{ES}] = \frac{1}{K_M} [\text{E}][\text{S}]$$

where

$$K_M = \frac{k_{-1} + k_2}{k_1} \quad [4]$$

- (b) Hence show that, within the steady state approximation, for a small initial enzyme concentration, $[\text{E}]_0$, the rate of the enzyme catalysed reaction is given by

$$R = \frac{d[\text{P}]}{dt} = \frac{V[\text{S}]}{K_M + [\text{S}]}$$

where $V = k_2[\text{E}]_0$. [6]

- (c) The oxidation of ethanol (S) to ethanal (P) is catalyzed in aqueous solution by alcohol dehydrogenase (E). The rate of reaction, R , at 298 K and fixed $[\text{E}]_0$, was found to vary with the concentration of substrate as follows:

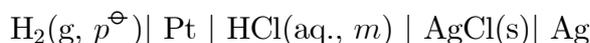
$[\text{S}]/\text{mol dm}^{-3}$	0.01	0.02	0.05	0.10
$R/10^{-3}\text{mol dm}^{-3}\text{s}^{-1}$	1.98	3.29	5.45	6.99

Determine the constant K_M . [5]

- (d) Draw a sketch to illustrate the variation of $[\text{S}]$, $[\text{ES}]$ and $[\text{P}]$ with time, assuming that the steady state approximation for $[\text{ES}]$ is valid. Is this likely to be the case for a small initial enzyme concentration, $[\text{E}]_0$? [5]

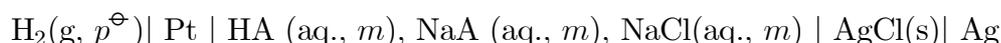
3. Electrochemical cells

- (a) Write down the cell reaction and the Nernst equation for the following cell, where m is the molality of HCl:



You may assume that H_2 gas behaves ideally. [4]

- (b) The dissociation constant of methanoic acid (HA) at 298 K can be determined from measurements of the emf, E , of the following cell:



The Nernst equation for this cell is identical with that for the cell in (a). Make a substitution for a_{H^+} and hence show that

$$\ln K = \frac{F}{RT} (E^\ominus - E) - \ln \frac{a_{\text{HA}} a_{\text{Cl}^-}}{a_{\text{A}^-}}$$

where K is the dissociation constant of the acid. [5]

- (c) A single measurement at $m = 0.0065 \text{ mol kg}^{-1}$ gave $E = 0.578 \text{ V}$ at 298 K. Assuming that all activity coefficients are unity, that methanoic acid is a weak acid, and that the standard potential of the half cell $\text{Cl}^- | \text{AgCl} | \text{Ag}$ is 0.222 V, calculate a value for K at this temperature. [5]

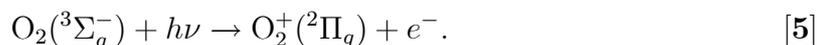
- (d) Measurements on the cell of part (b) at $m = 0.0065 \text{ mol kg}^{-1}$ and of the half-cell gave the results in the table below:

T/K	288	308
$E (\text{cell})/\text{V}$	0.571	0.580
$E^\ominus (\text{Cl}^- \text{AgCl} \text{Ag})/\text{V}$	0.227	0.212

Assuming that the activities do not change with temperature calculate the entropy of dissociation of the acid and comment on the result you obtain. [6]

4. Valence and Photoelectron Spectroscopy

- (a) Draw a molecular orbital energy level diagram of the O_2 molecule and use it to show that the first band in the photoelectron spectrum of ground state oxygen molecules (the band in which the photoelectron is ejected from the HOMO) gives rise to the electronic transition



- (b) This electronic band exhibits a vibrational progression with a vibrational spacing of $\nu \simeq 1900 \text{ cm}^{-1}$. Draw potential energy curves to illustrate the origin of this progression and discuss the fundamental physical principles involved. [5]

- (c) For sufficiently small displacements from its equilibrium bond length r'_e , the electronic potential energy curve $V(r)$ of $O_2(^2\Pi_g)$ can be approximated by that of a harmonic oscillator:

$$V(r) = V(r'_e) + \frac{1}{2}k(r - r'_e)^2.$$

Use this approximation to show that the most intense vibrational line in the first band of the O_2 photoelectron spectrum will occur at a vibrational quantum number v' satisfying

$$(v' + \frac{1}{2})\hbar\omega \simeq \frac{1}{2}k(r_e - r'_e)^2,$$

where $\omega = 2\pi c\nu$ is the vibrational frequency of O_2^+ and r_e is the equilibrium bond length of ground state O_2 . By considering the relationship between ω , k and the reduced mass μ of $^{16}O_2^+$, show that this rearranges to give

$$r'_e = r_e \pm \sqrt{\frac{\hbar}{\mu\omega}(2v' + 1)}. \quad [4]$$

- (d) Given that the most intense line in the observed spectrum has $v' = 1$, and that the equilibrium bond length of $O_2(^3\Sigma_g^-)$ is $r_e = 0.1208 \text{ nm}$, estimate r'_e . [4]
- (e) Discuss whether or not the electronic process in part (a) obeys the usual electric dipole selection rules for an electronic transition in a linear molecule. [2]

5. Surfaces

Answer **two** parts. All parts carry equal marks.:

- (a) At constant coverage, the enthalpy of adsorption, ΔH , is related to the equilibrium adsorption pressure, p , by

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\frac{\Delta H}{RT^2}.$$

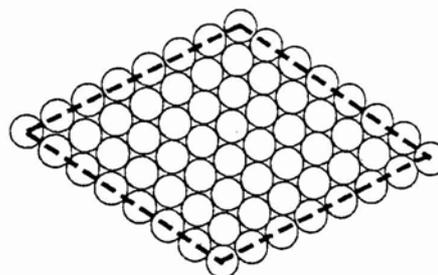
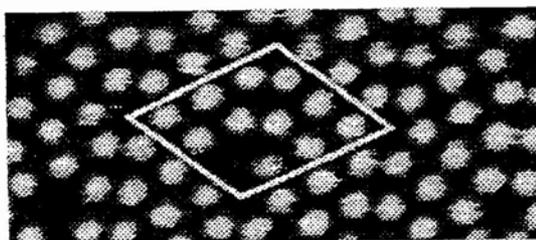
In the chemisorption of hydrogen on polycrystalline nickel the pressure required to give a particular coverage, θ , varied with temperature as follows:

p/mmHg	10^{-4}	1.7×10^{-3}	1.3×10^{-2}	0.11
T/K	223	250	273	303

Calculate ΔH for hydrogen on nickel at this coverage stating any assumptions you make. Explain why the value is likely to change with coverage.

Assuming that the hydrogen is dissociatively adsorbed and that its dissociation energy is 430 kJ mol^{-1} , estimate the energy of a surface NiH bond.

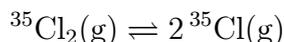
- (b) Explain the physical basis of scanning tunnelling microscopy (STM), using the STM image of the Silicon (111) surface shown below to illustrate your answer. The diamond-shaped outline in the STM image corresponds to the cell shown alongside for the idealized Si (111) surface.



- (c) When a mixture of either ethene and hydrogen or ethyne and hydrogen is adsorbed on platinum the same dominant surface species is obtained. In the reflection absorption infrared spectrum (RAIRS) three vibrational bands are observed in the region above 1000 cm^{-1} , at 2884 , 1339 and 1124 cm^{-1} . The first two decrease by a factor of $1/\sqrt{2}$ on deuteration but the last one is hardly affected. The selection rule for RAIRS is that only vibrations with a dipole change normal to the surface are allowed. Suggest a possible structure for the surface species that is consistent with these observations.

6. Statistical Mechanics

The equilibrium constant of the gas phase dissociation reaction



is given by statistical mechanics as

$$K_p = \frac{\left(q_{\text{Cl,m}}^{\ominus}/N_A\right)^2}{\left(q_{\text{Cl}_2,\text{m}}^{\ominus}/N_A\right)} e^{-\Delta_r E_0/RT}.$$

(a) Define the meaning of q_{m}^{\ominus} and $\Delta_r E_0$ in this expression. [2]

(b) Assuming that all the symbols have their usual meanings, use the data given below to calculate (i) $q_{\text{rot}} \simeq \frac{k_{\text{B}}T}{\sigma B}$ and (ii) $q_{\text{vib}} = (1 - e^{-h\nu/k_{\text{B}}T})^{-1}$ for Cl_2 , both at $T = 2000$ K:

$$\begin{aligned} ^{35}\text{Cl}_2: \quad \theta_{\text{rot}} &= B/k_{\text{B}} = 0.351 \text{ K} \\ \theta_{\text{vib}} &= h\nu/k_{\text{B}} = 805.3 \text{ K}. \end{aligned}$$

[3]

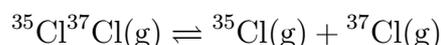
(c) Now calculate (i) q_{elec} for Cl, assuming that only states arising from the ground electron configuration need be retained, and (ii) $q_{\text{trans,m}}^{\ominus}/N_A$ for Cl_2 , again at 2000 K, using the following data:

$$\begin{aligned} ^{35}\text{Cl}: \quad \theta_{\text{elec}} &= [E(^2P_{1/2}) - E(^2P_{3/2})] / k_{\text{B}} = 1269 \text{ K}; \\ q_{\text{trans,m}}^{\ominus}/N_A &= 9.617 \times 10^8 \text{ at } 2000 \text{ K}. \end{aligned}$$

[5]

(d) Hence, given that $\Delta_r E_0 = 239.2 \text{ kJ mol}^{-1}$, complete the calculation of the equilibrium constant K_p at 2000 K. [4]

(e) Estimate the equilibrium constant of the reaction



at this temperature, and comment on the result you obtain. [3]

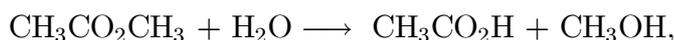
(f) Which of the various partition functions you calculated above will change in the presence of a magnetic field? Will $\Delta_r E_0$ also change? [3]

7. Solution Kinetics

- (a) The rate constant k of an activated chemical reaction in solution depends on pressure according to the equation

$$\ln k = \ln k_0 - \frac{p\Delta V^\ddagger}{RT}$$

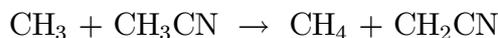
where k_0 is the value at zero pressure (approximately the same as at atmospheric pressure). For the following acid-catalysed hydrolysis in aqueous solution,



the rate of the reaction at 298 K increases by 35% when the pressure is increased from ambient (10^5 N m^{-2}) to 10^8 N m^{-2} . Calculate ΔV^\ddagger for the reaction. Given that the molar volume of $\text{CH}_3\text{CO}_2\text{CH}_3$ is $8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, comment on the implications of the observed value of ΔV^\ddagger for the mechanism of the reaction. [6]

- (b) The rate of diffusion of water and the conductivity of sodium ions in water both approximately double when the temperature is increased by about 40 K from room temperature. The viscosity of water approximately halves over the same temperature range. Comment. [6]

- (c) Methyl radicals generated in CH_3CN by γ -radiolysis react by the following process:

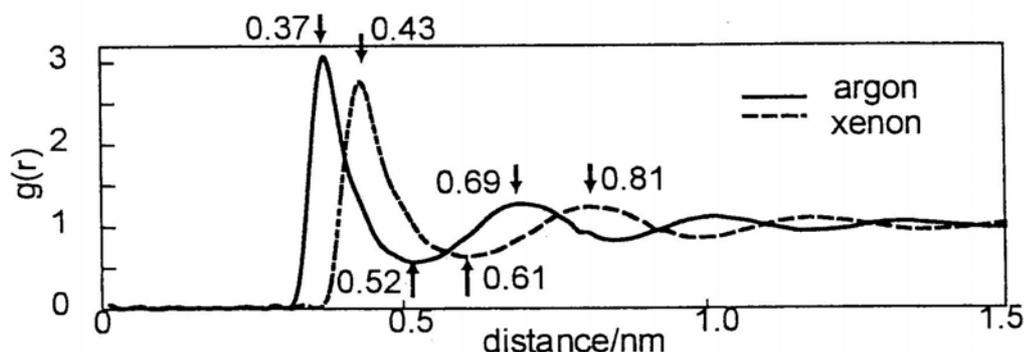


The equivalent reaction in CD_3CN is very much slower. Calculate the maximum expected value for the ratio $k_{\text{H}}/k_{\text{D}}$ at a temperature of 77 K assuming that only changes in zero point energy contribute to the difference in rate (the vibration of CH bond in CH_3CN occurs at a wavenumber of about 3000 cm^{-1}). [6]

The observed value of $k_{\text{H}}/k_{\text{D}}$ at 77 K is 2.8×10^4 . Discuss why this is larger than the value predicted from your calculation. [2]

8. Intermolecular Forces

- (a) Explain what is meant by the pair distribution function of a liquid. [2]
- (b) The pair distribution functions, $g(r)$, for the liquid states of Ar and Xe are shown in the diagram below. Comment on the main features of the two distributions (distances marked are in nm). [3]



- (c) The energy of interaction, $E(r)$, between a pair of inert gas atoms separated by a distance, r , is given approximately by

$$E(r) = -\frac{3\alpha'^2 I}{4r^6}$$

where the electronic polarizabilities α' (in appropriate units) and ionization potentials I of Ar and Xe are as given in the table below. Calculate the values of E for the two elements at the distance at which they are separated in the liquid. [7]

Inert gas	$I/\text{kJ mol}^{-1}$	α'/nm^3
Ar	1524	1.6×10^{-3}
Xe	1173	4.0×10^{-3}

- (d) The energy of vaporization, ΔU , of liquid xenon is 13.3 kJ mol^{-1} . Use the value of E for xenon from part (c) to estimate the coordination number in liquid xenon. [4]
- (e) For an equimolar mixture of Ar and Xe the internal energy of mixing, $\Delta_{\text{mix}}U$, is given approximately by $z\beta/4$ where z is the mean coordination number and

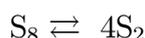
$$\beta = E_{\text{ArXe}} - \frac{1}{2}E_{\text{Ar}} - \frac{1}{2}E_{\text{Xe}}$$

where E_{Ar} and E_{Xe} indicate interactions between identical molecules and E_{ArXe} indicates the interaction between argon and xenon. An accurate estimate of E_{ArXe} is that it equals $-(E_{\text{Ar}}E_{\text{Xe}})^{1/2}$. Taking z to be 12, calculate the energy of mixing, $\Delta_{\text{mix}}U$, of equimolar argon and xenon. [4]

9. Thermodynamics: Miscellaneous

Derive any quantitative information and make as detailed comments as you can on **two** of the parts (a), (b) or (c). All parts carry equal marks.

- (a) At temperatures around 700 K the standard free energy change for the gas phase reaction



varies with temperature, T (in K), according to the equation:

$$\Delta G^\ominus / \text{kJ mol}^{-1} = 398.0 - 0.025T \ln T - 0.285T$$

- (b) The ideal solubility, x , of solid CBr_4 dissolved in an inert solvent varies with temperature (in K) in two different ways. At lower temperatures

$$\ln x = -\frac{818}{T} + 2.39$$

At higher temperatures

$$\ln x = -\frac{467}{T} + 1.29$$

- (c) (i) The osmotic pressure, Π/Pa , of a sample of poly(isobutene) in benzene at 300 K was found to vary with concentration, $c/\text{g dm}^{-3}$, below c of about 4 g dm^{-3} as

$$\Pi = 3.8c$$

- (ii) At 300 K and over a range of concentration of a surfactant in aqueous solution from its critical micelle concentration (CMC) to about $\text{CMC}/2$ the variation of surface tension, $\gamma/\text{N m}^{-1}$, with $\ln c$ was found to obey the equation

$$d\gamma = -0.01d \ln c$$