

DCHA 2706

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Friday, 31st May 2002, 2.30 p.m. to 5.30 p.m.

Answer *FIVE* out of nine questions

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

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

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

Fundamental Constants

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

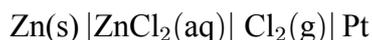
P^\ominus	=	1 bar = 10^5 Pa	1 atm = 101.325 kPa = 760 Torr
1 Da	=	1 g mol ⁻¹	1 L = 1 dm ³ 1 M = 1 mol L ⁻¹

1. Electrochemistry

State the relation between the reaction Gibbs energy $\Delta_r G$ and the cell EMF, E . Using this, obtain the Nernst equation for E , explaining carefully the meaning of all quantities involved. [4]

Explain how $\Delta_r H$ and $\Delta_r S$ may also be determined from electrochemical measurements. [4]

Under standard conditions, the EMF of the cell



is 2.120 V at $T=300$ K and 2.086 V at $T=325$ K. You may assume that ZnCl_2 is fully dissociated into its constituent ions.

(a) Write down the cell reaction, and explain why the above data enable the standard Gibbs energy of formation ($\Delta_f G^\ominus$) of $\text{ZnCl}_2(\text{aq})$ to be determined. [4]

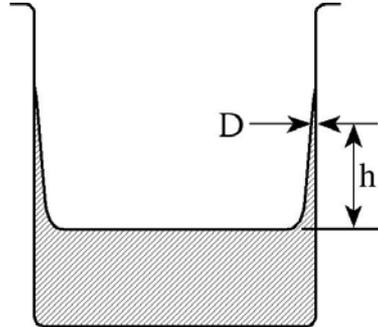
(b) Calculate the standard entropy ($\Delta_f S^\ominus$) and enthalpy ($\Delta_f H^\ominus$) of formation of $\text{ZnCl}_2(\text{aq})$ at $T = 300$ K. [4]

(c) Comment on the likely physical factors that determine the sign of $\Delta_f S^\ominus$. [4]

2. Molecular Interactions

(a) Explain, with examples, what is meant by the term *colloid*. [6]

(b) When octane is placed in a quartz vessel, the octane wets the walls of the vessel, as shown in the sketch below.



Within a continuum model, the energy, U , per unit area of a film of octane of thickness, D , due to van der Waals interactions is given by

$$U = -A/12\pi D^2$$

where the Hamaker constant $A = -7 \times 10^{-21}$ J.

The gravitational potential energy per unit area of the film at a height, h , above the liquid surface is given by

$$U = \rho g h D$$

where ρ is the density of the liquid and $g = 9.81 \text{ ms}^{-2}$ is the acceleration due to gravity.

(i) Sketch the form of each of these two potentials (for $A < 0$), and of their sum, as a function of D . [4]

(ii) Evaluate the equilibrium thickness of the film at $h = 1$ cm. (Take ρ to be 703 kg m^{-3} .) [4]

(c) The Hamaker constant for water interacting with itself across a vacuum is $A_{ww} = 3.7 \times 10^{-20}$ J while for a typical hydrocarbon oil, $A_{oo} = 5.1 \times 10^{-20}$ J.

(i) Estimate the Hamaker constant, A_{wo} , for water interacting with oil across a vacuum. [2]

(ii) Determine the sign of the Hamaker constant for a film of oil on water in air.

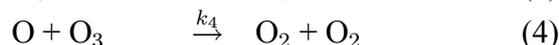
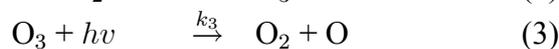
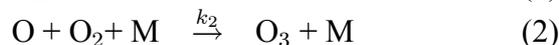
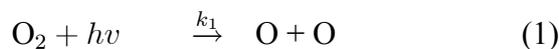
(You may use without proof the following combining relation for medium 1 interacting with

$$\text{medium 2 across medium 3: } A_{132} \approx A_{12} + A_{33} - A_{13} - A_{23}). \quad [2]$$

(iii) Hence predict whether oil will spread on water. [2]

3. Reaction Kinetics/Atmospheric Chemistry

The important 'oxygen-only' reactions in the stratosphere can be written



(a) Outline how this simple scheme predicts the formation of a layer of ozone. [3]

(b)(i) Under conditions of constant illumination, it is possible to write the rates of O atom production in photolysis steps (1) and (3) in the form $2k_1[\text{O}_2]$ and $k_3[\text{O}_3]$, where k_1 and k_3 have units of s^{-1} . Describe the factors which are likely to determine the magnitudes of k_1 and k_3 . [3]

(ii) Using the photolysis rate expressions in (i), write down the rate equations for O and O_3 . [2]

(iii) Under the conditions described in (i), use the steady state approximation to show that

$$[\text{O}][\text{O}_3] = \frac{k_1[\text{O}_2]}{k_4}.$$

With the help of this result and the rate equation for O_3 obtained in (ii), derive the following steady state expression for the ozone concentration

$$[\text{O}_3] = [\text{O}_2] \frac{k_1}{2k_3} (x - 1)$$

where

$$x = \sqrt{1 + 4k_2k_3[\text{M}]/(k_1k_4)}.$$

[9]

(c) In practice the above reaction scheme predicts significantly *greater* stratospheric ozone concentrations than those determined by direct measurement. Suggest an explanation for this discrepancy. [3]

4. Quantum Mechanics

State the Schrödinger equation for a one-dimensional quantum particle of mass m . [2]

What is Born's interpretation of the wavefunction $\Psi(x)$, and what conditions must $\Psi(x)$ satisfy to be physically acceptable? [4]

A particle is subject to the potential

$$V(x) = \begin{cases} \infty & : x < 0 \\ 0 & : 0 < x < L \\ V_0 & : x > L \end{cases}$$

with $V_0 > 0$.

(a) Sketch the potential. [1]

(b) Show that the wavefunction

$$\Psi(x) = \begin{cases} 0 & : x < 0 \\ A \sin(kx) & : 0 < x < L \\ B \exp(-k'x) & : x > L \end{cases}$$

satisfies the Schrödinger equation with energy $E < V_0$, provided $\hbar k = [2mE]^{1/2}$ and $\hbar k' = [2m(V_0 - E)]^{1/2}$. The constants A and B need not be determined. [4]

(c) Explain why $\Psi(x)$ is not physically acceptable unless $B = A \exp(k'L) \sin(kL)$. [2]

(d) Provide an argument to show that for $E < V_0$ the region $x > L$ is classically forbidden. [3]

(e) Show that the probability P_f that the particle is found in the classically forbidden region is $P_f = A^2 \sin^2(kL)/(2k')$; and that the expectation value of the kinetic energy is $E - V_0 P_f$. You may assume that A has been chosen so that $\Psi(x)$ is normalized. [4]

5. Photochemistry

With the aid of a diagram, describe briefly the major radiative and non-radiative pathways available to an electronically excited molecule in solution. [4]

Answer the following questions:

(a) A solution of the laser dye rhodamine 6G in methanol has a fluorescence lifetime of 5 ns, and a fluorescence quantum yield of 0.87.

Determine the radiative and non-radiative rate constants. [5]

(b) Benzene in a solution with hexane has a fluorescence lifetime of 5.5 ns. The fluorescence lifetime is approximately halved on addition of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ of biacetyl.

Calculate the quenching rate constant for biacetyl with electronically excited benzene. [4]

(c) A solution of Br_2 in CCl_4 contained in a cell of 2.0 mm thickness has a transmittance of 0.356 at a Br_2 concentration of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$. CCl_4 is transparent at the wavelength employed for the measurement.

Determine the molar absorption coefficient of Br_2 . State any assumptions you make. [3]

(d) In the gas phase photodissociation of HBr at 193 nm, H atoms are generated with a two-component velocity distribution, peaking at $2.27 \times 10^4 \text{ m s}^{-1}$ and $2.07 \times 10^4 \text{ m s}^{-1}$.

Estimate the dissociation energy of HBr and the spin-orbit splitting in Br. [4]

[You may assume that $m_{\text{H}} = 1.0 \text{ u}$, and that $m_{\text{Br}} \gg m_{\text{H}}$, and hence you can ignore the kinetic energy of the Br atom.]

6. Thermodynamics

State how the entropy change of a substance is related to the reversible heat absorbed by it. [2]

(a) Using the first and second laws of thermodynamics, show that

$$dG = VdP - SdT; \quad [4]$$

and that

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T. \quad [3]$$

(b) By considering the entropy as a function of P and T , show that

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_p}{T}dT$$

where C_p is the constant pressure heat capacity. [4]

(c) Hence determine the reversible heat liberated when the pressure acting on a 10 cm^3 block of Cu is increased from 1 bar to 100 bar under isothermal conditions at $T = 298 \text{ K}$. For Cu, the expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = 5 \times 10^{-5} \text{ K}^{-1}$; it may be assumed to be constant, and the pressure dependence of V may be neglected. [4]

(d) Using the Clausius inequality for dS , explain why the amount of heat liberated in reality cannot be less than the above estimate. [3]

7. Infrared Spectroscopy

(a) Sketch the normal vibrational modes of CO_2 and identify the symmetry species of each mode. [4]

(b) The low resolution IR absorption spectrum of CO_2 has two prominent bands: the band centred at 667 cm^{-1} has P, Q and R branches while the band near 2350 cm^{-1} has only P and R branches. Assign these bands to the correct normal modes, justifying your choice. [4]

(c) Explain why only even J levels exist in the $v = 0$ state of $^{12}\text{C}^{16}\text{O}_2$. [3]

(d) The wavenumbers (in cm^{-1}) of the lines nearest one of the band centres of $^{12}\text{C}^{16}\text{O}_2$ are

2353.1 2351.6 2350.1 2347.7 2346.1 2344.5

Estimate the rotational constant and determine the band centre, $\tilde{\nu}_0$. (You may neglect the difference between the rotational constants in the $v = 0$ and $v = 1$ states). [4]

(e) Describe qualitatively how the IR absorption spectra of

(i) $^{13}\text{C}^{16}\text{O}_2$

(ii) N_2O

would differ from that of $^{12}\text{C}^{16}\text{O}_2$. [5]

(Nuclear spin quantum numbers, I , are ^{12}C : $I = 0$, ^{13}C : $I = \frac{1}{2}$, ^{16}O : $I = 0$)

8. Statistical Mechanics

Statistical mechanics gives the following result for the equilibrium constant K ($\equiv K_P$) of a gas phase reaction:

$$K = \prod_J \left[\frac{q_J}{N_A} \right]^{\nu_J} \exp(-\Delta E_0/RT)$$

- (a) Explain carefully the meaning of the quantities appearing in this expression. [3]

Consider the thermal ionization of an atomic species A,



with ionization energy I . For both A and A^+ , you need retain only the lowest energy electronic state ^{2S+1}L arising from the appropriate ground electronic configuration; the difference in energy between the spin-orbit components (J) of these states may be neglected.

- (b) Show that the equation for this equilibrium (the Saha equation) may be expressed as

$$K = \frac{2k_B T}{P^\ominus \Lambda^3(T)} \frac{g_{A^+}}{g_A} \exp(-I/RT)$$

where $\Lambda(T)$ is the de Broglie wavelength of the electron, and g_{A^+} and g_A denote respectively the degeneracies of the A^+ and A electronic ground states. [7]

Note that for a particle of mass m , the translational partition function is given by $q_{tr} = V/\Lambda^3(T)$, where $\Lambda(T) = h/[2\pi mk_B T]^{1/2}$.

- (c) Calculate K at $T = 4000$ K for the thermal ionization of carbon atoms. For C, $I = 1086$ kJ mol $^{-1}$. [7]

(d) In assuming Boltzmann statistics, the above result for K effectively treats the electrons as classical particles. This is valid only if $\Lambda(T) \ll (V/N_e)^{1/3}$ where N_e/V is the number density of electrons. For $T = 4000$ K and $P/P^\ominus = 10^{-4}$, the fraction of ionized carbon atoms is 1.7×10^{-4} .

Can the quantum mechanical nature of the electrons be neglected under these conditions? Explain your reasoning. [3]

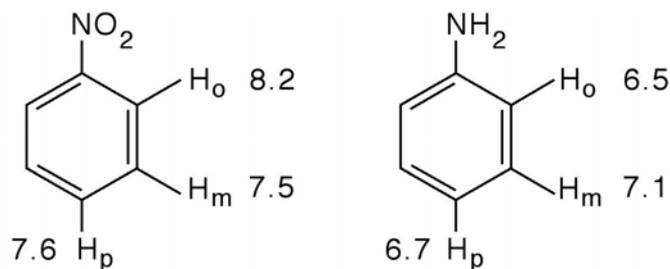
9. NMR

(a) Define the chemical shift parameter, δ , in NMR. [2]

(b) Describe the main factors affecting the chemical shifts of protons in molecules in solution. [6]

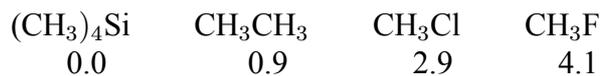
(c) Comment on the chemical shift values for the protons indicated in the molecules below.

(i)



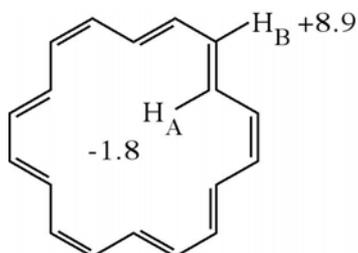
(Note that δ for the protons in benzene is 7.3) [4]

(ii)



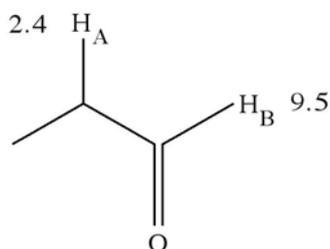
[3]

(iii)



[2]

(iv)



[3]