

DCHA 2706

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Monday, 7th June 2004, 2.30 p.m. to 5.30 p.m.

Answer *FIVE* out of eight questions

Please begin your answer to each question on a new page.

The numbers in square brackets indicate the approximate marks 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	$2.998 \times 10^8 \text{ m s}^{-1}$
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}	$= 1 \text{ bar} = 10^5 \text{ Pa}$	$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr}$
m^{\ominus}	$= 1 \text{ mol kg}^{-1}$	$1 \text{ L} = 1 \text{ dm}^3$
1 Da	$= 1 \text{ g mol}^{-1}$	$1 \text{ M} = 1 \text{ mol L}^{-1}$

1. Atomic Spectroscopy

The energy levels of atoms can often be described by the formula

$$E_{n,\ell} = -\mathcal{R}/(n - \delta_\ell)^2.$$

Define the symbols in this equation. [2]

The lowest terms and ionization energies (E_i) of the atoms Li and Li^{++} , measured in cm^{-1} relative to the ground states, are:

	${}^7\text{Li}$	${}^7\text{Li}^{++}$
$1s$		0.0
$2s$	0.0	740 733.6
$2p$	14 903.66	740 731.2
$3s$	27 206.12	877 916.6
$3p$	30 925.38	877 915.9
$3d$	31 283.08	877 927.6
E_i	43 487.19	987 657.8

Comment on the following properties of these energy levels:

- (a) The $3s$, $3p$ and $3d$ terms of Li^{++} are almost degenerate, whereas they are widely separated for Li. [4]
- (b) The value for E_i of Li^{++} is much larger than that of H ($109\,678.8\text{ cm}^{-1}$). [3]
- (c) The spin-orbit splitting of Li in its $2p$ term is 0.337 cm^{-1} (very similar to that for the H atom) whereas it is 29.58 cm^{-1} in the corresponding term of Li^{++} . [3]
- (d) The value for E_i of ${}^7\text{Li}^{++}$ is 12.85 cm^{-1} larger than that of ${}^6\text{Li}^{++}$. [4]

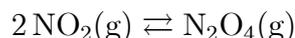
Use the data above to evaluate the quantum defects for the ${}^7\text{Li}$ atom in s , p and d orbitals; you may assume that $\mathcal{R} = \mathcal{R}_\infty$. Comment on your results. [4]

$$[m({}^6\text{Li}) = 6.015\text{ u}, m({}^7\text{Li}) = 7.016\text{ u}, m_e = 0.5484 \times 10^{-3}\text{ u}, \mathcal{R}_\infty = 109\,737.15\text{ cm}^{-1}]$$

Turn over.

2. Thermodynamics

- (a) Show from first principles how (i) the enthalpy, and (ii) the entropy of a substance vary with temperature at constant pressure. [4]
- (b) Explain what is meant by the standard Gibbs energy of formation of a compound. [2]
- (c) At $T = 298$ K, the standard molar Gibbs energies of formation of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are respectively $\Delta_f G^\circ = 51.31$ kJ mol⁻¹ and 97.89 kJ mol⁻¹. The standard enthalpy change for the reaction



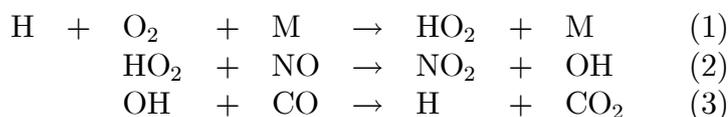
is $\Delta_r H^\circ = -57.2$ kJ mol⁻¹ at $T = 298$ K. The molar heat capacities of NO_2 and N_2O_4 are given respectively by $C_{p,m} = 37.2$ J K⁻¹ mol⁻¹ and 77.3 J K⁻¹ mol⁻¹; they may be assumed to be temperature independent.

For this reaction, calculate the equilibrium constant $K(T)$ and the entropy change $\Delta_r S^\circ$ at $T = 298$ K. [4]

- (d) Derive the van't Hoff equation for $d \ln K(T)/dT$. [4]
- (e) Using the data given in part (c) determine $\Delta_r H^\circ$, $\Delta_r G^\circ$ and $\Delta_r S^\circ$ for the reaction at $T = 400$ K. Comment fully on the values you obtain. [6]

3. Atmospheric Chemistry and Applied Kinetics

- (a) What chemical processes are primarily responsible for the formation of O_3 and OH radicals in the troposphere? [2]
- (b) Draw up a chemical reaction scheme showing the elementary steps involved in the oxidation of methane in the troposphere, starting with the attack of OH radicals on the hydrocarbon. Identify all radicals and other intermediates that appear in your scheme. [4]
- (c) Explain the role of the oxides of nitrogen ($NO_x = NO_2 + NO$) in the oxidation scheme of part (b). [2]
- (d) The reactions



are the most important in determining the ratio $[OH]/[HO_2]$ in the troposphere. What is meant by 'M' in equation (1), and what part does it play in the reaction? [2]

Calculate the steady-state concentration of HO_2 for an air parcel in which $[OH] = 1.6 \times 10^6$ molecule cm^{-3} , $[CO] = 3 \times 10^{12}$ molecule cm^{-3} and $[NO] = 1 \times 10^9$ molecule cm^{-3} , given that $k_2 = 8.1 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$ and $k_3 = 2.4 \times 10^{-13}$ cm^3 molecule $^{-1}$ s $^{-1}$. (k_2 and k_3 are the rate coefficients for reactions (2) and (3)). Assume that reaction (1) is sufficiently rapid in the regions of the atmosphere under discussion to convert H to HO_2 'instantaneously'. [5]

- (e) The rate coefficient for the reaction of OH with CH_4 is 4.0×10^{-15} cm^3 molecule $^{-1}$ s $^{-1}$ at the average temperature of the troposphere (277 K). Calculate the lifetime in years of methane in the atmosphere. Assume that $[OH]$ is constant during the day, and averaged over a 24-hour period (day **and** night) is half that given in part (d). [2]

Measurements of methane in the atmosphere show that it is present at a volume mixing ratio (mole fraction) of 1.7×10^{-6} . Assuming that the total mass of air in the troposphere is 4.5×10^{18} kg, and that the average molar mass of air is 28.8 g mol $^{-1}$, estimate the source strength (annual release) of CH_4 in units of kg yr $^{-1}$. State **one** natural and **one** anthropogenic (man-made) source of the hydrocarbon. [3]

Turn over.

4. Valence

- (a) The ground electronic configuration of CO₂ is written ... $\sigma_g^2 \sigma_u^2 \pi_u^4 \pi_g^4$. What electronic state arises from this configuration? Give the spectroscopic term symbol. [2]
- (b) The π_x molecular orbitals in this description of CO₂ can be expressed as linear combinations of the $2p_x$ atomic orbitals on the C and O atoms, of the form

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

where the atoms are labelled O₁ – C₂ – O₃. An equivalent degenerate set arises for a linear combination of $2p_y$ atomic orbitals. If ϕ_1 , ϕ_2 and ϕ_3 are orthonormal functions, the secular equations which define these π molecular orbitals are given by

$$\begin{bmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{21} & H_{22} - E & H_{23} \\ H_{31} & H_{32} & H_{33} - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

(where all matrix elements are taken to be real).

Using the symmetry of the CO₂ molecule to relate certain matrix elements, and approximating H_{13} to zero, show that the eigenvalues for these equations are:

$$\begin{aligned} E_1 &= \frac{1}{2}(H_{11} + H_{22}) - \frac{1}{2}[(H_{11} - H_{22})^2 + 8H_{12}^2]^{1/2} \\ E_2 &= H_{11} \\ E_3 &= \frac{1}{2}(H_{11} + H_{22}) + \frac{1}{2}[(H_{11} - H_{22})^2 + 8H_{12}^2]^{1/2} \end{aligned}$$

Show the relative energies of these orbitals in a qualitative sketch. [7]

- (c) Derive the values for the coefficients c_1 , c_2 , c_3 , for the eigenvalue E_2 and sketch the form of this molecular orbital. Without going into details, sketch the form of the molecular orbital corresponding to E_1 . [5]
- (d) In the photoelectron spectrum of CO₂, the first two peaks occur at 13.79 and 17.32 eV. Use your previous results to identify the ionization processes involved and predict the qualitative vibrational structure associated with these two processes. [3]
- (e) In the electronic spectrum of CO₂⁺, the lowest energy transition is assigned as $^2\Pi_u - ^2\Pi_g$. Predict the wavelength of the (0–0) band in this transition. Would you expect there to be extensive vibrational structure associated with this transition? [3]

$$[1 \text{ eV} \equiv 8065.5 \text{ cm}^{-1}]$$

5. Molecular Interactions

The Lennard-Jones potential between two closed-shell atoms can be written as

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$

- (a) Sketch the potential and explain the physical significance of the parameters σ and ε . [4]
- (b) Describe the physical interactions that give rise to the two terms in the pair potential. [4]
- (c) Why does a repulsive contribution of the form $\exp(-r/\sigma)$ provide a more realistic approximation than does the repulsive term in the Lennard-Jones potential? [2]
- (d) Show that the minimum in $U(r)$ occurs at $r_e = 2^{1/6}\sigma$. [2]
- (e) Show that, to leading order in $(r - r_e)$, the Taylor expansion of $U(r)$ is

$$U(r) = U(r_e) + \frac{1}{2} \left(\frac{\partial^2 U}{\partial r^2} \right)_{r=r_e} (r - r_e)^2$$

and use this result to show further that the force constant, k , for a pair of atoms in a Lennard-Jones potential well is given by

$$k = \frac{72\varepsilon}{(2)^{1/3}\sigma^2}. \quad [5]$$

- (f) Using the value of k obtained in part (e) above, and assuming simple harmonic oscillator behaviour, calculate the fundamental vibrational frequency of a $^{131}\text{Xe}_2$ molecule, given that $\varepsilon = 2.8 \times 10^{-21}$ J and $\sigma = 0.43$ nm for Xe. [3]

Turn over.

6. Polymers/Solution Thermodynamics

- (a) Simple thermodynamic arguments can be used to show that for dilute, ideal solutions of solutes possessing a single molar mass, the osmotic pressure Π is given by the expression

$$\Pi = \frac{1000 RT}{M} c$$

where the concentration c is in units of kg m^{-3} (g dm^{-3}), and M is the molar mass of the solute *in conventional gram units* (relative to $^{12}\text{C} = 12 \text{ g mol}^{-1}$).

Measurement of the osmotic pressure is one method used to determine the molar mass of polymers. Explain why it is appropriate to replace M in the equation by M_n , where M_n is the number-average molar mass of the polymer. Give an equation that defines M_n . [4]

- (b) A sample of poly(ethylene) was separated into five fractions possessing different ranges of molar masses. The masses of the fractions obtained are shown in the table.

Molar mass range/ 10^5 g mol^{-1}	0.5–1.5	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5
Mass of sample/g	10.23	5.15	1.44	0.34	0.06

From these data, estimate M_n for the sample. [6]

- (c) For dilute polymer solutions, the deviation from ideality is such that the osmotic pressure has to be written as a virial expansion

$$\frac{\Pi}{c} = \frac{1000 RT}{M_n} (1 + Bc + \dots)$$

The table below shows values of the osmotic pressure for a solution of a given sample of poly(styrene) at two different temperatures.

	$c/\text{kg m}^{-3}$	1.0	2.0	3.0	5.0
$T=320 \text{ K}$	$\Pi/\text{N m}^{-2}$	28.1	59.2	93.3	170.5
$T=330 \text{ K}$	$\Pi/\text{N m}^{-2}$	30.1	65.8	107.0	205.7

By plotting a suitable graph, find M_n for the polymer and values for the second virial coefficient, B , at the two temperatures. [7]

- (d) Explain why B might vary with temperature and, assuming that B varies linearly with temperature over the range 300 to 340 K, calculate the temperature at which its value is zero for poly(styrene) in cyclohexane. [3]

7. Statistical Mechanics

(a) The deuterium nucleus is a boson with nuclear spin $I = 1$. Explain what is meant by this statement, including the factors that determine whether a given nucleus is a boson or a fermion. [5]

(b) The joint rotational–nuclear spin contribution to the molecular partition function of the D_2 molecule is

$$q_{\text{rot;ns}} = n_+ \sum_{J \text{ even}} (2J + 1) \exp(-\theta_r J(J + 1)/T) \\ + n_- \sum_{J \text{ odd}} (2J + 1) \exp(-\theta_r J(J + 1)/T)$$

where $n_+ = 6$ and $n_- = 3$ denote respectively the number of symmetric and antisymmetric nuclear-spin states. Provide a full justification for this expression. [6]

(c) *ortho*- D_2 (*para*- D_2) molecules have even (odd) J -levels occupied. Show that the equilibrium constant $K(T) = N_{\text{para}}/N_{\text{ortho}}$ is given by

$$K(T) = \frac{n_- \sum_{J \text{ odd}} (2J + 1) \exp(-\theta_r J(J + 1)/T)}{n_+ \sum_{J \text{ even}} (2J + 1) \exp(-\theta_r J(J + 1)/T)} \quad [4]$$

(d) The characteristic rotational temperature of D_2 is $\theta_r = 85$ K. Calculate $K(T)$ at $T = 85$ K, and determine its leading asymptotic behaviour at high and low temperatures. Sketch the overall T -dependence of $K(T)$ and explain in physical terms why $K(T) \rightarrow 0$ as $T \rightarrow 0$. [5]

Turn over.

8. Surfaces

- (a) The principal features of chemisorption are expected to be well described by the Langmuir adsorption isotherm

$$\theta = \frac{KP}{1 + KP} \quad (1)$$

where P is the pressure of the gas and K is independent of pressure. Derive this equation, stating clearly the assumptions on which it is based. Why does the Langmuir isotherm fail to describe the characteristics of physisorption? [5]

- (b) Carbon monoxide is found to adsorb on the (111) surface of a particular transition metal single crystal. N , the number of CO molecules adsorbed per square metre, is measured as a function of CO gas pressure, P_{CO} , at 400K. The results are presented in the table below:

$P_{\text{CO}}/10^{-4}$ Pa	0.44	1.7	4.0	9.3
$N/10^{18}\text{m}^{-2}$	0.80	2.4	4.0	5.6

- i. Show that the data conform to the Langmuir isotherm equation (1) above. Calculate the values for K and for N_{∞} , the maximum surface concentration of CO which can be chemisorbed. [7]
- ii. At a higher temperature of 420K, a pressure of 5.6×10^{-3} Pa is required to achieve the highest fractional coverage given in the table above. Define the enthalpy of adsorption $\Delta_{\text{ads}}H$ of CO and calculate its value at this particular surface concentration. (You may assume that $\Delta_{\text{ads}}H$ is independent of temperature). [4]
- iii. Describe briefly the experimental techniques which can be used to investigate the atomic structure of the metal surface and of the adsorbed CO. [4]

End of Examination