

XCHA 2716

SECOND PUBLIC EXAMINATION
Honour School of Natural Science

CHEMISTRY PART 1A

PHYSICAL CHEMISTRY 1A

TRINITY TERM 2005

Thursday, 9th June, 2005, 9.30 a.m. to 12.30 p.m.

Candidates should answer *five* questions

Please start each question in a new booklet.

The numbers in square brackets indicate the approximate marks that examiners intend to assign to each part of the question.

Attention is drawn to the table of constants provided on page 2 of this booklet.

Guide to Questions

- | | |
|--------------------------|-------------------------------|
| 1. Thermodynamics | 5. Valence |
| 2. Liquids and solutions | 6. Statistical thermodynamics |
| 3. Spectroscopy | 7. Kinetics |
| 4. Quantum Mechanics | 8. Miscellaneous |

Do not open the paper until you are told to do so.

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	$= 1 \text{ g mol}^{-1}$	$1 \text{ M} = 1 \text{ mol L}^{-1}$
0°C	$= 273.15 \text{ K}$	

1. Thermodynamics

- (a) Starting from the expression $dG = Vdp - SdT$ show that for an ideal gas, i , the chemical potential is given by

$$\mu_i = \mu_i^\ominus + RT \ln(p_i/p^\ominus)$$

Define clearly all symbols. [2]

- (b) Write an expression for the equilibrium constant, K_p , for the gas phase reaction



in terms of the partial pressures of the reactant (A) and the products (B and C). [2]

- (c) Use the result in (a) to show how K_p is related to the standard molar Gibbs energy change for the reaction. [4]
- (d) How and why would the expression for K_p in (b) change if A and B were solids? [2]
- (e) Silver carbonate decomposes on heating:



Calculate the equilibrium constant at 110 °C given the following data

	$Ag_2CO_3(s)$	$Ag_2O(s)$	$CO_2(g)$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-501.4	-29.07	-393.5
$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$	167.3	121.7	213.7
$C_p / \text{J K}^{-1} \text{ mol}^{-1}$	109.6	68.6	37.1

where $\Delta_f H^\ominus$ is the standard enthalpy of formation (298 K), S^\ominus is the absolute entropy (298 K) and C_p is the heat capacity. [8]

- (f) Using your result in (e) explain why if a sample of silver carbonate is dried in an oven at 110 °C decomposition can be prevented by the presence of ca 1% by volume of carbon dioxide in the atmosphere. [2]

Turn over.

2. Liquids and solutions

Answer either (A) or (B)

Either

(A) (a) The Debye-Hückel limiting law is

$$\log_{10}\gamma_{\pm} = -A |z_+z_-| \sqrt{I}$$

where A is a constant. Define the other terms in the equation and summarise succinctly the physical model used to derive this equation, pointing out any assumptions made. [7]

(b) Use the equation in (a) to derive the following expression for the solubility, S, of a salt, MX in terms of its solubility product, K_{sp} and the total ionic strength of the solution:

$$\log_{10}S = \frac{1}{2} \log_{10}K_{sp} + a\sqrt{I}$$

Give an expression for the positive constant a. [4]

(c) The solubility of silver iodate has been studied in water and in aqueous solutions of potassium nitrate at 298 K. The following data were measured.

[KNO ₃]/10 ⁻³ M	0.0	1.301	3.252
[AgIO ₃]/10 ⁻⁴ M	1.771	1.823	1.870

By plotting a suitable graph determine the following quantities:

- (i) The constant A in the Debye-Hückel limiting law,
- (ii) the solubility product of silver iodate,
- (iii) the mean activity coefficient, γ_{\pm} , of silver iodate in pure water. [9]

Or

(B) (a) Starting from the definition of chemical potential

$$\mu_i = \mu_i^* + RT \ln x_i$$

where x is the mole fraction, prove that the osmotic pressure, Π , of an ideal solution of concentration, c (g L^{-1}), is given by

$$\Pi/c = RT/M$$

where M is the relative molecular mass of the solute. [9]

(b) For polymer and other solutions, expressions of the following type may be obeyed

$$\Pi/c = RT[(1/M) + Ac + \dots]$$

where A is a constant. Comment. [1]

(c) Osmotic pressure studies on solutions of haemoglobin at 280 K yielded the following data

[Haemoglobin]/ g L ⁻¹	10	20	30	60	90
Osmotic pressure/ cm H ₂ O	3.47	7.20	11.17	24.60	40.50

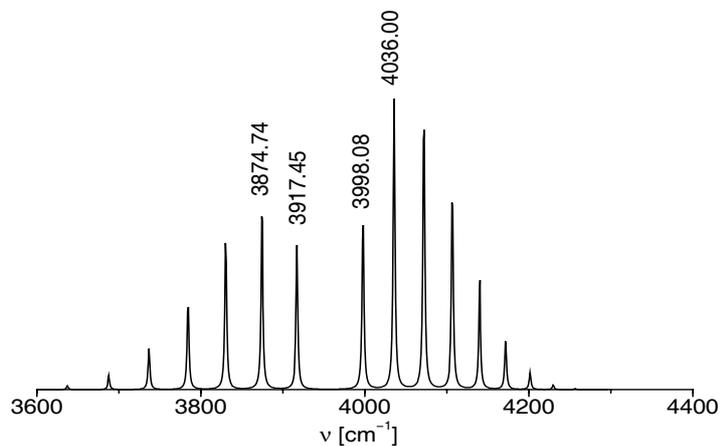
By plotting a suitable graph calculate the relative molecular mass of haemoglobin ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 84.7 \text{ L cm H}_2\text{O mol}^{-1} \text{ K}^{-1}$). **[10]**

Turn over.

3. Spectroscopy

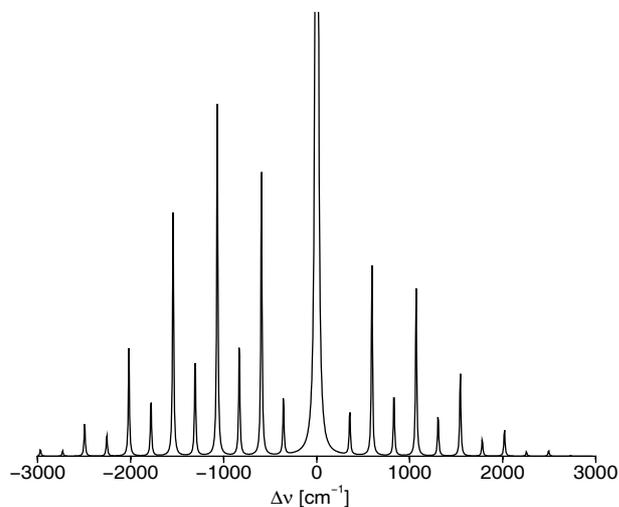
Answer either (a) or (b)

(a) The following figure shows the IR absorption spectrum of HF.



- i. Discuss the selection rules that lead to this spectrum. [6]
- ii. Use the method of combination differences and the wavenumbers given in the figure to calculate the rotational constants B_0 and B_1 of HF. [6]
- iii. Now use the formula $B_v = B_e - \alpha_e(v + 1/2)$ to calculate the equilibrium rotational constant B_e , and hence the equilibrium bond length r_e , of the molecule ($\hbar/4\pi c\mu = 17.61 \text{ \AA}^2 \text{ cm}^{-1}$ for HF). [4]
- iv. How would you expect the IR spectrum of DF to differ from that of HF? (Relative atomic masses: H = 1.0, D = 2.0, F = 19.0.) [4]

- (b) The following figure shows the rotational Raman spectrum of H_2 at 1000 K as a function of the wavenumber difference $\Delta\nu = \nu_f - \nu_i$, where ν_i and ν_f are the wavenumbers of the incident and scattered radiation.



- i. Discuss the selection rules that lead to this spectrum. [6]
- ii. Explain why the intensity alternates between consecutive lines in the spectrum. [6]
- iii. By assigning the peak close to $\Delta\nu = -2000 \text{ cm}^{-1}$ or otherwise, estimate the rotational constant B_0 of H_2 , and use this to obtain an estimate for the average bond length of the molecule ($\hbar/4\pi c\mu = 33.45 \text{ \AA}^2 \text{ cm}^{-1}$ for H_2). [6]
- iv. How would you expect the intensity pattern in the spectrum to change if the temperature were lowered to 300 K? [2]

Turn over.

4. Quantum Mechanics

The vibrational Schrödinger equation of a diatomic molecule can be approximated by

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] \psi(x) = E\psi(x),$$

where $x = r - r_e$ is the displacement of the bond length from its equilibrium value.

- i. Define the symbols μ and k in this equation, and explain why it is only an approximation to the full vibrational Schrödinger equation of a diatomic molecule. [4]
- ii. Find α for which the wavefunction

$$\psi(x) = e^{-\alpha x^2/2}$$

is a solution of the equation, and determine the corresponding energy eigenvalue E in terms of μ and k . [8]

- iii. Find the values of x for which

$$-\frac{\hbar^2}{2\mu\psi(x)} \frac{d^2\psi(x)}{dx^2} = 0,$$

and comment on the physical significance of these values. [4]

- iv. Use the fact that

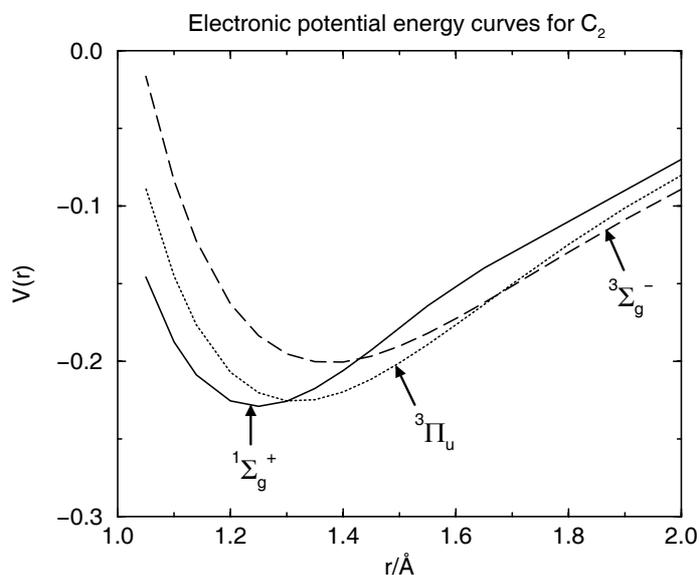
$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

to determine the expectation values of the potential energy and the kinetic energy for the wavefunction $\psi(x)$. [4]

5. Valence

Answer (a) and either (b) or (c)

- (a) Outline the basis of the LCAO-MO theory of chemical bonding, and give an example of a situation in which this theory breaks down. [6]
- Construct molecular orbital energy level diagrams for C_2 and Si_2 , and use these diagrams to show that the ground electronic states of these molecules are $^1\Sigma_g^+$ and $^3\Sigma_g^-$, respectively. [8]
 - Within the Born-Oppenheimer approximation, the identity of the lowest electronic state of a diatomic molecule can change as a function of its bond length, as illustrated for the case of C_2 in the following figure



Use your molecular orbital energy level diagrams for C_2 and Si_2 and your understanding of valence to explain why the lowest electronic state of C_2 changes from $^1\Sigma_g^+$ to $^3\Pi_u$ and then to $^3\Sigma_g^-$ as the bond length r increases. Hint: Start by identifying the electron configurations of these three electronic states. [6]

Question continues...

Turn over.

- (c) i. Sketch the linear combinations of the two hydrogen 1s orbitals in a symmetric linear AH₂ molecule that transform like the σ_g and σ_u irreducible representations of the $D_{\infty h}$ point group. [2]
- ii. By combining these two symmetry-adapted linear combinations with the 2s and 2p orbitals of the A atom, construct a molecular orbital energy level diagram in $D_{\infty h}$ symmetry for a first-row AH₂ triatomic, assuming that the ionization potential of H(1s) is similar to that of A(2p). [4]
- iii. Use the following descent in symmetry table to construct a Walsh diagram showing how the molecular orbital energy levels of AH₂ change as the H–A–H bond angle decreases from 180°. [4]

$$\begin{array}{c|ccc} D_{\infty h} & \sigma_g & \sigma_u & \pi_u \\ \hline C_{2v} & a_1 & b_2 & a_1 + b_1 \end{array}$$

- iv. The first and second electronic absorption bands of the water molecule correspond to the promotion of electrons from different occupied orbitals into the same unoccupied orbital. Each of these absorption bands leads to an electronically excited water molecule, H₂O*, which subsequently dissociates into OH + H. A key experimental observation is that the OH product molecule obtained from the second absorption band has more rotational excitation (reflecting more bending excitation in H₂O*) than that from the first. Use your Walsh diagram to rationalize this observation and identify the orbital excitations that are responsible for the two bands. [4]

6. Statistical Thermodynamics

Answer either (a) or (b)

- (a) The quantum mechanical energy levels ε_n and degeneracies g_n of a doubly-degenerate bending vibration are given within the harmonic normal mode approximation by $\varepsilon_n = (n + 1)h\nu$ and $g_n = (n + 1)$ where $n = 0, 1, 2, \dots$

- i. Use the fact that $1 + 2x + 3x^2 + \dots = (1 - x)^{-2}$ for $|x| < 1$ to sum the expression for the molecular partition function

$$q = \sum_{n=0}^{\infty} g_n e^{-\beta\varepsilon_n}$$

of this vibration, and compare your result with the partition function of a non-degenerate oscillator, $q = e^{-\beta h\nu/2}(1 - e^{-\beta h\nu})^{-1}$. [4]

- ii. The contribution of the vibration to the average energy per molecule in a system of N non-interacting molecules is given by

$$\frac{E}{N} = -\frac{1}{q} \frac{dq}{d\beta},$$

where $\beta = 1/k_B T$. Show that, for the doubly-degenerate oscillator,

$$\frac{E}{N} = h\nu [1 + 2e^{-\beta h\nu}(1 - e^{-\beta h\nu})^{-1}],$$

and demonstrate that this expression yields a contribution of $2R$ to the molar heat capacity in the limit as $\beta h\nu \rightarrow 0$.

Hint: $e^{-x} \simeq 1 - x$ for small x . [8]

- iii. According to the Boltzmann distribution law, the probability that a molecule will be found in the n -th quantum level is

$$P_n = \frac{g_n e^{-\beta\varepsilon_n}}{q}.$$

Use this formula to obtain an expression for the most populated level n of the degenerate bending vibration at temperature T . [4]

- iv. The most populated level of the bending vibration of CO_2 in an oxygen-acetylene flame was inferred from IR hot band intensity measurements to be $n = 2$. Given that $\bar{\nu} = 667.3 \text{ cm}^{-1}$ for CO_2 , estimate the temperature of the flame. ($hc/k_B = 1.438 \text{ K cm.}$) [4]

Question continues...

Turn over.

- (b) The equilibrium constant for a gas phase chemical reaction can be written in terms of molecular partition functions as

$$K_p = \prod_J \left[\frac{q_m^\ominus(J)}{N_A} \right]^{\nu_J} e^{-\Delta E^0/RT}$$

where the product \prod_J is taken over all species J in the reaction.

- i. Write down the equilibrium constant K_p for the thermal ionization equilibrium



in terms of the partition functions $q_m^\ominus(\text{Cs})$, $q_m^\ominus(\text{Cs}^+)$ and $q_m^\ominus(e^-)$ and the ionization potential I of Cs. [4]

- ii. What are the electronic partition functions of Cs, Cs^+ , and e^- ? Show that these electronic partition functions cancel in the expression for K_p , and explain why the expression can be further simplified to

$$K_p = \left[q_{\text{trans},m}^\ominus(e^-)/N_A \right] e^{-I/RT}. \quad [4]$$

- iii. Recalling that $q_{\text{trans},m}^\ominus(e^-) \simeq V_m^\ominus/\Lambda_e^3$, where V_m^\ominus is the standard molar volume and $\Lambda_e = h/\sqrt{2\pi m_e k_B T}$ is the thermal wavelength of an electron, show that K_p can be written in the form

$$K_p = AT^{5/2} e^{-I/RT},$$

where A is independent of T . Hence evaluate K_p at $T = 2000$ K given that $A = 3.34 \times 10^{-7} \text{ K}^{-5/2}$ and $I = 375 \text{ kJ mol}^{-1}$. [6]

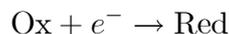
- iv. Use your value for K_p to calculate the fraction of ionized Cs atoms at $T = 2000$ K when $p = 10^{-3} p^\ominus$, and hence estimate the average distance between neighbouring electrons under these conditions. How does the Coulomb interaction energy $V(r) = e^2/4\pi\epsilon_0 r$ at this distance compare with $k_B T$? ($e^2/4\pi\epsilon_0 = 2.31 \times 10^{-28} \text{ J m}$.) [6]

7. Kinetics

Answer either (a) or (b) or (c)

(a) *Either*

- i. Write an account of cyclic voltammetry. Include a detailed description of the form of the current-voltage curve seen for the process



when both Ox and Red are stable. Explain what is seen if Red is unstable and how the kinetics of its decay could be investigated. Illustrate how cyclic voltammetry is used to obtain information about electrode reaction mechanisms. [12]

- ii. The Butler-Volmer equation for the Faradaic current, I , due to the reduction of a species Ox at an electrode can be written

$$I \propto [\text{Ox}] \exp\{-(\alpha F/RT)(E - E^\circ)\}$$

E° is the standard potential of the redox couple, F is the Faraday constant and only Ox is assumed to be present in solution. Explain the significance of the parameter α .

The following current - voltage (I/E) data were recorded at a carbon electrode for the one electron reduction of Ce(IV) in aqueous solution at 298 K

E/mV	1436	1416	1396	1376
$I/\mu\text{A}$	305	475	725	1130

By means of a suitable plot determine the value of α for the Ce(IV)/Ce(III) couple. [$RT/F = 25.7 \text{ mV}$ at 298 K] [8]

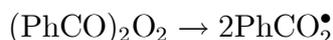
(b) *Or*

Give an account of the transition state (activated complex) theory of chemical kinetics, highlighting its strengths and weaknesses.

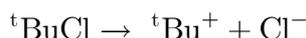
[20]

(c) *Or*

- i. What do you understand by the term volume of activation, ΔV^\ddagger , for a reaction in solution? For the reaction



in tetrachloromethane solvent, ΔV^\ddagger is $10 \text{ cm}^3 \text{ mol}^{-1}$, whereas for the reaction

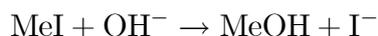


in EtOH/ H_2O , ΔV^\ddagger is $-16 \text{ cm}^3 \text{ mol}^{-1}$. Comment. [6]

Question continues...

Turn over.

- ii. The rate constant for the reaction



increases continuously by almost a factor of 10^6 on going from pure solvent water to almost pure dimethylsulphoxide (DMSO), which has a high dielectric constant (relative permittivity). Comment.

Predict whether the activity coefficient of OH^- is bigger or smaller in DMSO than in water. [6]

- iii. The second order rate constant for the reaction



has a value of $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 298 K. The autoprotolysis constant, K_w , for water at this temperature has the value of 1.0×10^{-14} . Calculate the half life of H_2O before ionization. [8]

8. Miscellaneous

Answer 3 of the following.

Each part carries equal weight

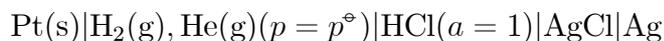
[Total marks: 20]

- (a) The ratio of the heat capacities, C_p/C_v , for He has a value of 1.66 and is independent of temperature. Comment as fully as you can.
- (b) Both H atoms and He^+ ions show lines in their emission spectra close to the following wavelengths: 121.50 nm, 102.51 nm, 97.20 nm. Comment.
[$R_\infty = 109,737 \text{ cm}^{-1}$]
- (c) The spatial parts of two approximate wavefunctions for the 1s2s electron configuration of the helium atom are

$$\Psi_{\pm}(r_1, r_2) = (1/\sqrt{2})[1s(r_1)2s(r_2) \pm 1s(r_2)2s(r_1)]$$

Which of the two wavefunctions Ψ_{\pm} can be combined with a triplet spin state and which with a singlet spin state? What are the corresponding spin wavefunctions?

- (d) For He, the equation of state is of the form $p(V - b) = RT$. Comment on the origin of the non-ideality in He. The molar volume of He at 100 atmospheres and 273 K is 0.011075 of its molar volume at 1 atmosphere pressure and 273 K. Estimate the radius of the He atom. [$RT = 22.414 \text{ L atm}$ at 273 K]
- (e) Predict the EMF of the following electrochemical cell



at 298 K when the hydrogen/helium gas mixture contains (i) 10% and (ii) 1% of hydrogen given that the standard electrode potential of the Ag/AgCl couple is 0.2223 V. In each case, state which is the positive, and which the negative electrode. [$RT/F = 25.7 \text{ mV}$ at 298 K]

End of Examination