

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Friday, 6 June 1997, 2.30 p.m. to 5.30 p.m.

Candidates should answer *five* questions

The numbers in square brackets indicate the weight the examiners expect to assign to each part of the question.

Speed of light, c	$= 2.9979 \times 10^8 \text{ m s}^{-1}$
Planck's constant, h	$= 6.6261 \times 10^{-34} \text{ J s}$
Boltzmann's constant, k_B	$= 1.3807 \times 10^{-23} \text{ J K}^{-1}$
Molar gas constant, R	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro's constant, N_A	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, F	$= 96487 \text{ C mol}^{-1}$
RT/F	$= 0.02567 \text{ V at } 298 \text{ K}$
Atomic mass unit, u	$= 1.66054 \times 10^{-27} \text{ kg}$

1. a) Given the rotational constants, B_v , listed below:

- (i) Explain the differing values of B_v for H^{35}Cl in ($v = 0$) and ($v = 1$). [3]
- (ii) Calculate the equilibrium bond length, r_e , for H^{35}Cl . [2]
- (iii) Compare the *inverse* ratio of reduced masses for H^{35}Cl and D^{35}Cl with the ratio of ($v = 0$) rotational constants for these molecules and comment on why these are not equal. [3]

	B_v / cm^{-1}
H^{35}Cl ($v = 0$)	10.440
H^{35}Cl ($v = 1$)	10.138
D^{35}Cl ($v = 0$)	5.399

(Relative atomic masses: $^1\text{H} = 1.008$, $^2\text{D} = 2.014$, $^{35}\text{Cl} = 34.969$)

b) The harmonic vibrational frequencies of H^{35}Cl and D^{35}Cl are given below.

	$\omega_e / \text{cm}^{-1}$
H^{35}Cl	2990.946
D^{35}Cl	2145.163

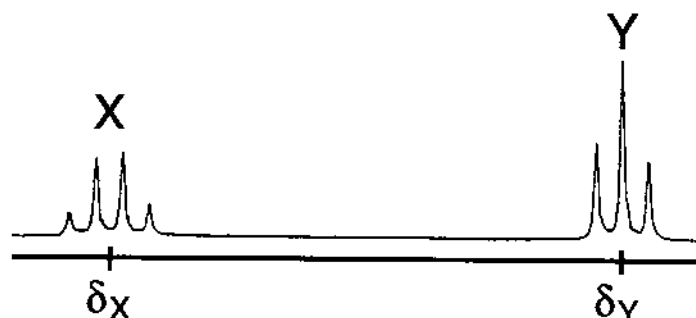
Determine the ratio of the force constants for these molecules and comment on your answer. [3]

- c) The rotational Raman spectra of H^{35}Cl and D^{35}Cl were recorded using an excitation vacuum wavelength of 514.5 nm. Predict the *absolute* wavenumbers (in cm^{-1}) for the scattered radiation in the first three anti-Stokes lines of H^{35}Cl (i.e., those closest to the excitation wavenumber). [4]
- d) The most intense Raman anti-Stokes line in the spectrum of H^{35}Cl occurs when the upper level of the transition has a J value given by the formula

$$J_{\max} = \sqrt{\frac{k_B T}{2B_0 hc}} - \frac{1}{2}$$

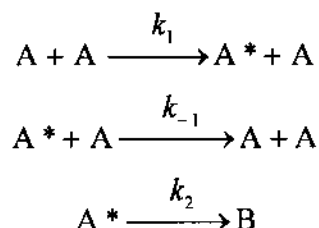
Explain the origin of this formula. [5]

2. The ^1H NMR spectrum of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ is shown below:



- a) Define the term *chemical shift* in an NMR spectrum and explain why the peaks labelled X in the spectrum have a different chemical shift from the peaks labelled Y. ($\delta_X = 3.36$, $\delta_Y = 1.16$.) [4]
- b) The peaks labelled Y occur at a mean frequency of 60.0150696 MHz in a fixed field B_0 ; calculate the mean frequency of the peaks X at the same field. [3]
- c) Describe the mechanism that gives rise to nuclear spin-spin coupling and explain why the presence of 10 protons in $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ gives rise to only 7 peaks in the spectrum with the intensity ratios 1:3:3:1 and 1:2:1 as shown. [6]
- d) If the magnetic field B_0 is doubled in magnitude compared with that used to obtain the data in a) and b), calculate the new frequencies for each of the four peaks labelled X in the spectrum of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, given that the splitting between the peaks labelled Y is 7.2 Hz. [4]
- e) The broadband decoupled ^{13}C NMR spectrum of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ shows two peaks with chemical shifts of 67.4 and 17.1. Comment on why the range of ^{13}C chemical shifts is so much greater than that for the proton NMR chemical shifts of the same compound. [3]

3. a) Derive an equation for the rate of conversion of A into B according to the following reaction scheme. [4]



- b) Explain why so-called unimolecular reactions that follow this scheme display a change in kinetics from 1st order to 2nd order overall as the pressure is lowered and why the addition of inert gas can significantly influence the reaction rate. [3]
- c) The *cis-trans* isomerisation of an alkene was studied as a function of pressure at constant temperature, and the following *effective* first-order rate constants were measured.

concentration $\times 10^6 / \text{mol dm}^{-3}$	4.0	7.0	14.0	65.0
rate constant $\times 10^5 / \text{s}^{-1}$	1.28	1.47	1.69	1.89

- (i) Show that the reaction kinetics, over the given concentration range, are consistent with the reaction scheme in a). [4]
- (ii) Calculate k_f and the limiting value of the effective first-order rate constant at high pressures. [4]
- (iii) Explain why the reaction kinetics associated with many unimolecular reactions deviate significantly from the quantitative predictions of the reaction scheme in a). [5]

4. What is meant by the terms *intersystem crossing*, *excimer fluorescence* and *triplet-triplet annihilation*? [3]

Account for the following observations:-

- a) When a dilute solution of pyrene (a polynuclear, aromatic hydrocarbon) in ethanol is exposed to ultra-violet light, it emits a violet fluorescence. Sudden extinction of the ultra-violet source results in the near instantaneous (sub-microsecond) extinction of almost all the fluorescence but, at high light intensities, in de-oxygenated solutions, the fluorescence decay also displays a delayed component.

In a concentrated solution, the violet fluorescence is replaced by an intense, sky-blue luminescence, which decays near instantaneously when the excitation source is extinguished.

When the concentrated solution is cooled, becoming increasingly viscous and eventually forming a glass, the violet fluorescence returns as the sky-blue luminescence fades. Sudden extinction of the ultra-violet source again results in the near-instant loss of the fluorescence but, in the glassy solution, a red 'after-glow' remains, decaying with a half-life ca. 1 s. [8]

- b) Hydrogen iodide presents a broad, continuous absorption spectrum in the ultra-violet, peaking at a wavelength ca. 220 nm. When the vapour is exposed to a laser flash, at a wavelength of 248 nm, it is possible to detect H atoms recoiling from the irradiation zone; the atoms display a bimodal velocity distribution with peak velocities at 13.6 km s^{-1} and 19.2 km s^{-1} . [9]

The bond dissociation energy, $D_0(\text{H-I}) = 298 \text{ kJ mol}^{-1}$;

Relative atomic masses; H = 1.008, I = 126.9;

The spin-orbit splitting for iodine ($^2\text{P}_{1/2} - ^2\text{P}_{3/2}$) = 91 kJ mol^{-1} .

$1 \text{ kJ mol}^{-1} \equiv 83.594 \text{ cm}^{-1}$.

5. a) Explain why the activity coefficients of ions in dilute aqueous solutions are generally less than 1.0. Discuss the physical basis of any equations you quote.

[4]

- b) The table below gives the solubility of AgCl in H₂O/KNO₃ solution at 298K. By using a suitable extrapolation procedure, determine the solubility product of AgCl.

[6]

$m(\text{KNO}_3) \times 10^3 / \text{mol kg}^{-1}$	$m(\text{AgCl}) \times 10^5 / \text{mol kg}^{-1}$
4.11	1.381
8.35	1.420
13.71	1.453
20.12	1.488

- c) Write down the cell reaction corresponding to the cell diagram below, and using your result from b), predict the standard EMF for the cell at 298K.

[4]



- d) If an external EMF were applied to the cell above, so as to make the left hand electrode more negative than the equilibrium value, in which direction would the cell reaction proceed?

[2]

- e) Discuss the qualitative form of the current versus overvoltage plot for the Ag/Ag⁺ electrode under steady state conditions; contrast it with the equivalent plot for the liberation of H₂ at a silver electrode, given that the exchange current densities for the Ag/Ag⁺ and the H₂/H⁺ equilibria at a silver electrode are $1.3 \times 10^{-2} \text{ A cm}^{-2}$ and $4.0 \times 10^{-7} \text{ A cm}^{-2}$, respectively.

[4]

6. a) The Schrödinger Equation for a particle confined to a ring of radius r and subject to a constant potential V may be written in the form:

$$\left[\frac{-\hbar^2}{2I} \frac{d^2}{d\phi^2} + V \right] \Psi = E\Psi$$

where I is the moment of inertia of the particle.

Show by direct substitution that $\Psi = N e^{im\phi}$ is a solution of the Schrödinger Equation (where N and m are constants) and, by applying the boundary conditions, determine the quantised values of energy. [4]

- b) If Ψ is an eigenfunction of the operator $\hat{\Omega}$ with eigenvalue ω , show that the expectation value of that operator is equal to ω . [3]

- c) A linear combination of the form

$$\Psi' = Ae^{i\phi} + Be^{-i\phi}$$

where A and B are non-zero constants, is a solution of the Schrödinger Equation above, and is an eigenfunction of the l_z^2 operator, but is not an eigenfunction of the l_z operator ($l_z = -i\hbar d/d\phi$).

- (i) Determine the expectation value, $\langle l_z^2 \rangle$, for the function Ψ' .
- (ii) Show that the normalisation integral for Ψ' is equal to $2\pi (A^2 + B^2)$.
- (iii) Determine the ratio of the coefficients A/B if the expectation value $\langle l_z \rangle = \hbar/3$.

What would be the quantum mechanical uncertainty in the measurement of l_z ? [8]

- d) When an electron confined to a ring interacts with radiation polarised in the x direction, the transition dipole operator is of the form

$$\mu = \mu_0 \cos(\phi) \quad [= \frac{1}{2} \mu_0 (e^{i\phi} + e^{-i\phi})]$$

Show that the integral

$$\int_0^{2\pi} e^{-im'\phi} e^{i\phi} e^{im\phi} d\phi$$

is equal to zero unless $m' = m - 1$, and hence deduce that the selection rules for transitions induced by this radiation between the states of the electron confined to the ring are $\Delta m = \pm 1$. [5]

7. a) Outline experimental evidence which demonstrates that molecules may dissociate when adsorbed on a metal surface. [4]
- b) The rates of hydrogen adsorption (R_{ads}) and desorption (R_{des}) at a Pt surface in a gaseous hydrogen environment can be expressed in the forms

$$R_{ads} = A(1 - \theta)^2 p_{H_2}$$

$$R_{des} = B \exp(-E / RT)\theta^2$$

where E is a constant, p_{H_2} is the pressure of hydrogen, θ is the fraction of occupied adsorption sites, T is the temperature, and A and B are parameters that vary slowly with temperature.

Suggest physical explanations and interpretations for the forms of these equations and for the parameter E . [4]

- c) Show that the isotherm describing the variation of θ with p_{H_2} has the form

$$\theta = \frac{X p_{H_2}^{\frac{1}{2}}}{1 + X p_{H_2}^{\frac{1}{2}}}$$

where $X = \left(\frac{A}{B}\right)^{\frac{1}{2}} \exp(E / 2RT)$. [6]

- d) If nitrogen is added to the gas phase, ammonia is produced as a result of a reaction between adsorbed nitrogen and hydrogen species on the Pt surface at a rate given by the equation

$$R_{NH_3} = \frac{C p_{N_2} p_{H_2}^{\frac{1}{2}}}{(1 + D p_{H_2}^{\frac{1}{2}})^2}$$

R_{NH_3} describes the initial rate of formation of ammonia, p_{N_2} is the nitrogen pressure and C and D are temperature dependent parameters.

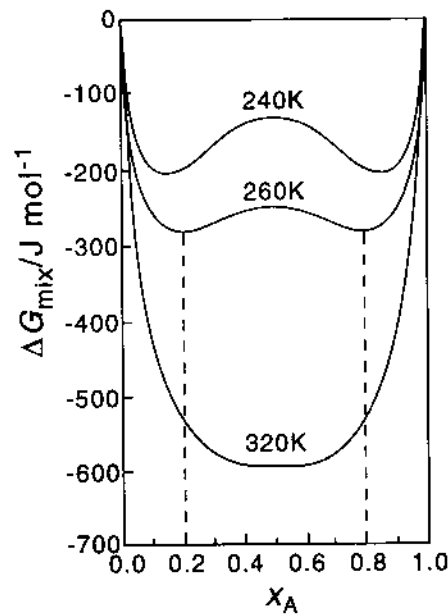
Give a physical interpretation for the form of the above equation. [6]

8. a) Show how the enthalpy of mixing, ΔH_{mix} , in a *regular* solution of two components, A and B, may be related to the pairwise interactions between its components, H_{AA} , H_{BB} , and H_{AB} , via an equation of the form

$$\Delta H_{\text{mix}} = \beta x_A x_B$$

where β depends on H_{AA} , H_{BB} , and H_{AB} . [4]

- b) Why would you not expect mixtures of (i) water and benzene, and (ii) water and polystyrene, to behave like regular solutions? Under what conditions might the solution in example (ii) show ideal behaviour? [6]
- c) The figure below shows a plot of the free energy of mixing, ΔG_{mix} , for a two-component system, over the full range of molar compositions, $x_A = 0 \rightarrow 1$ and a range of temperatures.



- (i) Over what range of compositions will the mixture be immiscible when the temperature is 260 K?
- (ii) At this temperature, the mixture was found to behave as a regular solution. Write down expressions for ΔG_{mix} , and $(\partial \Delta G_{\text{mix}} / \partial x_A)_T$ in terms of x_A ; hence calculate the enthalpy of mixing of the two components at the composition $x_A = 0.1$.
- (iii) Calculate the upper critical solution temperature of the mixture, assuming the solution remains *regular* up to this temperature. [10]