

SECOND PUBLIC EXAMINATION
Honour School of Natural Science

CHEMISTRY PART IB

PHYSICAL CHEMISTRY

OPTION 2

SAMPLE PAPER

Two hours

Candidates should answer *two* questions.

The numbers in square brackets indicate the approximate marks which 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.

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

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

1.

- (a) Draw a molecular orbital (MO) diagram for the OH radical, and use it to predict the ground electronic state of the radical. In drawing your diagram you need only consider the $2p$ levels of oxygen, which you can assume lie lower in energy than the H atom $1s$ orbital. [5]
- (b) In the gas phase, the OH radical in its ground electronic state is often detected by observing fluorescence induced by laser excitation to the lowest excited state, which has ${}^2\Sigma$ symmetry. Use your MO diagram to identify the likely electronic configuration of this excited state. [4]
- (c) Explain briefly what is meant by vibrational predissociation. OH in the lowest excited ${}^2\Sigma$ state undergoes predissociation above the vibrational level $\nu' = 1$, which becomes increasingly rapid with increasing ν' . What effect would this predissociation have on the fluorescence quantum yield, the observed fluorescence lifetime, and the linewidths of resolved rovibronic transitions? [6]
- (d) How would you expect the linewidths of transitions to levels with $\nu' \leq 1$ to vary with temperature and total pressure? Explain your reasoning. [4]
- (e) Electronically excited OH(${}^2\Sigma$) also undergoes rapid electronic quenching with certain molecules. How does the presence of a quencher gas affect the observed fluorescence rate constant?

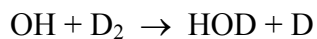
The following table shows OH(${}^2\Sigma$) $\nu' = 0$, observed fluorescence lifetimes, τ_{obs} , as a function of water concentration. Employ a graphical procedure to obtain the quenching rate constant for OH(${}^2\Sigma$) with water, and its radiative lifetime in the $\nu' = 0$ vibrational level.

$[\text{H}_2\text{O}] / (10^{15} \text{ molecule cm}^{-3})$	0.5	1.0	1.5	2.0	2.5
$\tau_{\text{obs}} / \text{ns}$	710	620	540	490	440

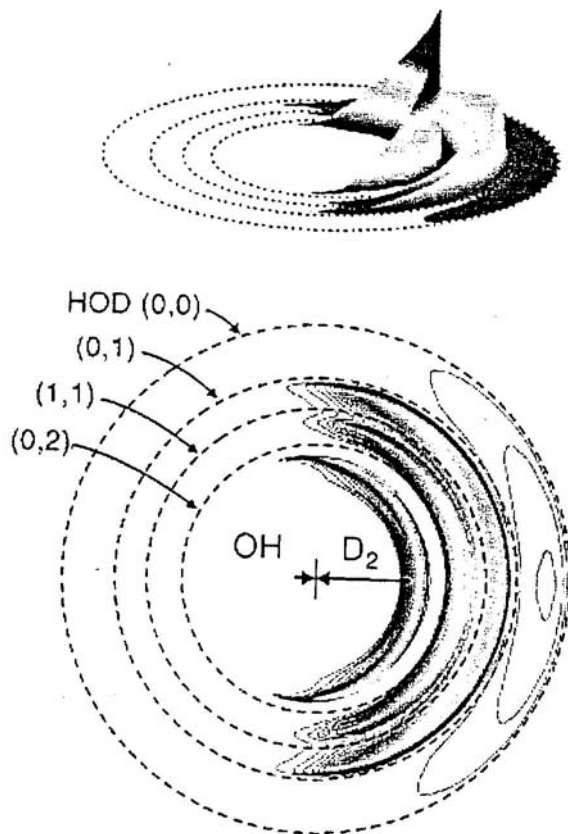
How would you expect the quenching rate constant to compare qualitatively with that for OH(${}^2\Sigma$) with a rare gas? [8]

Question continues

(f) OH in its ground electronic state undergoes the reaction



which is isoelectronic with the $\text{F} + \text{H}_2$ reaction. The figures below show plots of product flux in the centre-of-mass frame for the above reaction. The experiments were performed under molecular beam conditions, with the D atom products detected by a laser ionization technique.



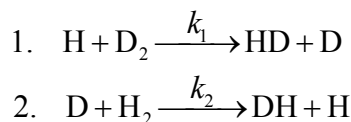
The dashed rings are labelled according to the number of quanta m in the bending mode, and n in the OD stretching mode of $\text{HOD}(m, n)$.

- (i) What does the above figure suggest about the mechanism of the reaction?
- (ii) What spectroscopic experiments might be performed to probe the transition state region of this reaction (or a similar reaction) more directly? [7]

2.

(a) Explain what is meant by *kinetic isotope effect* and how it is related to zero point energy. [4]

(b) Consider the following gas-phase reactions:

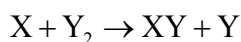


Estimate the ratio of the rate constants k_2/k_1 at 300 K using the vibrational wavenumbers given below. Assume that the effect of isotopic substitution is limited to changes in the zero point energies of reactants and transition states, and that the transition states are linear.

	H ₂	reaction 1 transition state	reaction 2 transition state
stretch (cm ⁻¹)	4395	1762	1773
bend (doubly degenerate) (cm ⁻¹)	-	694	870

(1 cm⁻¹ ≡ 11.96 kJ mol⁻¹) [8]

(c) For the reaction of an atom X with a diatomic molecule Y₂



proceeding through a linear transition state, Transition State Theory gives

$$k = \frac{k_B T}{h} \frac{q_{\text{int}}^{\ddagger}}{q_t q_{\text{X,int}} q_{\text{Y}_2,\text{int}}} \exp(-\varepsilon_0 / k_B T)$$

where $q_{\text{X,int}}$ and $q_{\text{Y}_2,\text{int}}$ are the partition functions for the internal modes (rotational, vibrational, electronic) of the reactants and q_t is related to the masses of the reactants by

$$q_t = \left(\frac{2\pi k_B T}{h^2} \frac{m_X m_{\text{Y}_2}}{m_X + m_{\text{Y}_2}} \right)^{3/2}$$

Question continues

Outline the origin of the expression for k (no derivations are required), comment on the assumptions involved, and explain the meaning of the symbols q_{int}^\ddagger and ε_0 .

[8]

- (d) Show that the expression for k in (c) leads to the following equation, stating and justifying the assumptions and approximations used.

$$\frac{k_2}{k_1} = \frac{m_D}{m_H} \frac{I_2^\ddagger}{I_1^\ddagger} \left(\frac{m_D + 2m_H}{m_H + 2m_D} \right)^{3/2} \exp[-(\varepsilon_{0:2} - \varepsilon_{0:1})/k_B T]$$

The 1,2 subscripts refer to the two reactions in (b) and I^\ddagger denotes the moment of inertia of the transition state.

[8]

- (e) Hence obtain a revised estimate of k_2/k_1 at 300 K.

[3]

Note. $I_1^\ddagger = 4.02 \times 10^{-47} \text{ kg m}^2$, $I_2^\ddagger = 3.95 \times 10^{-47} \text{ kg m}^2$.

The relative atomic masses of H and D are 1 and 2 respectively.

- (f) The experimental value of k_2/k_1 is 14 at 300 K. Why is this value larger than that predicted by Transition State Theory?

[3]

3.

A pulsed electrical discharge in a mixture of CO₂, N₂ and He at atmospheric pressure is used to create a population inversion and hence lasing action on the (0,0,1)-(1,0,0) band of CO₂.

- (a) Explain the collisional processes between N₂ and CO₂ which lead to the population inversion. The (0,1,0), (1,0,0) and (0,0,1) energy levels of CO₂ are at 667, 1388 and 2284 cm⁻¹, and N₂ ($\nu = 1$) is at 2331 cm⁻¹. [4]

- (b) The (0,0,1) level has ¹Σ_u⁺ symmetry. Explain the meaning of this symbol, and draw an energy level diagram for the rotational states J' in this upper vibrational level for the ¹²C¹⁶O₂ isotopomer. Remember ¹⁶O has nuclear spin $I = 0$.

The rotational degrees of freedom in the ¹Σ_u⁺ (0,0,1) upper state can be represented by a temperature of 400 K, and the most populated rotational level is $J' = 19$. Use this to estimate the value of the rotational constant B in the (0,0,1) state. [7]

- (c) Spontaneous emission in the (0,0,1)-(1,0,0) band which originates from $J' = 19$ occurs as two lines at 944.194 and 974.622 cm⁻¹. Identify these lines, explain the origins of the selection rules for the transitions, and deduce the value of the rotational constant B in the (1,0,0) level. You may neglect centrifugal distortion. [4]

- (d) Laser gain α is given by the equation

$$\alpha = K \frac{S_J}{\nu^3} \left[\frac{N'}{g'} - \frac{N''}{g''} \right]$$

where K is a constant, S_J a line strength factor equal to $J' + 1$ for a P branch transition and J' for an R branch transition, ν is the transition frequency and N' , N'' are populations in the upper and lower levels respectively, with degeneracies g' and g'' .

Show that if N'' is zero the gain will be larger on the P branch transition for a given J' . How might a laser cavity be constructed to ensure that lasing occurs on the R branch transition? [4]

Question continues

(e) The (1,0,0) lower lasing level is metastable with respect to radiative processes. Explain why this is, and give an account of the detailed processes for population losses in the (1,0,0) level. [4]

(f) The lowest frequency vibration-rotation absorption band of CO₂ (starting from the ground state) occurs with P, Q and R branches. The first three P branch lines are at the following wavenumbers: 665.820, 664.263, 662.710 cm⁻¹.

Explain why there is P, Q and R branch structure, assign quantum numbers to the three P branch lines and from their wavenumbers calculate the rotational constants B in the ground and first vibrationally excited states, again neglecting centrifugal distortion. Comment on the relative values of B for these states and for the value in the (1,0,0) state that you have calculated above. [7]

(g) From your value of B for the ground state calculate the CO bond length in CO₂. Explain why your value is an approximation, and suggest how it could be improved. [4]

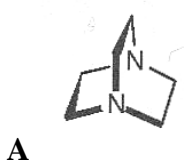
4.

- (a) Discuss the differences between ^1H NMR and EPR in the light of the different values of the gyromagnetic ratios γ_{H} and γ_{e} . You may wish to include some of all of the following in your discussion:

populations of energy levels, sensitivity, spin-spin coupling, spin relaxation, linewidths, spectral resolution, time resolution, applications.

$$\gamma_{\text{H}} = +2.675 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}; \quad \gamma_{\text{e}} = -1.761 \times 10^{11} \text{ T}^{-1} \text{ s}^{-1} \quad [14]$$

- (b) The 9.25 GHz EPR spectrum of the radical $\text{HO}-\bullet\text{CH}-\text{COOH}$ in aqueous solution comprises four lines at field positions $3298.160 \pm 0.985 \text{ mT}$ and $3298.160 \pm 0.725 \text{ mT}$. Explain the appearance of this spectrum by means of an energy level diagram. [5]
- (c) Explain why the EPR spectrum of the cation radical ($\text{A}^{\bullet+}$) of the molecule **A** comprises 65 lines whose positions relative to the centre of the spectrum can be predicted by means of just two hyperfine coupling constants. [5]



Spin quantum numbers: $^{14}\text{N}, I = 1$; $^1\text{H}, I = \frac{1}{2}$, $^{12}\text{C}, I = 0$.

- (d) Hydrogen atoms in the gas phase can be detected using radiofrequency radiation with a wavelength of 21 cm. Predict the appearance of the EPR spectrum of hydrogen atoms in a 9 GHz spectrometer and estimate the field positions of the lines. [5]

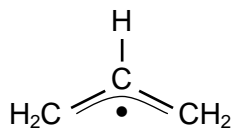
Note. The resonance condition for an electron coupled to a nucleus with magnetic quantum number m_I is

$$\nu = \frac{\gamma_{\text{e}} B}{2\pi} + m_I a$$

where B is the magnetic field strength, a is the hyperfine coupling constant and ν is the spectrometer frequency.

Question continues

- (e) Comment on the observation that the EPR spectrum of the allyl radical displays hyperfine coupling constants of 1.48 mT (2 protons); 1.39 mT (2 protons); 0.41 mT (1 proton) in the light of the Hückel theory π -molecular orbitals given below. [5]



$$\frac{1}{2}(\phi_1 \pm \sqrt{2}\phi_2 + \phi_3); \quad \varepsilon = \alpha \pm \sqrt{2}\beta$$

$$\frac{1}{\sqrt{2}}(\phi_1 - \phi_3); \quad \varepsilon = \alpha$$

5.

Explain with the aid of energy level diagrams the necessary condition for laser action.

[4]

For three of the following lasers:

- (i) He/Ne or Ar⁺
- (ii) Ruby or Nd/YAG
- (iii) Dye
- (iv) Excimer, e.g. XeCl
- (v) Chemical laser, e.g. HCl

explain how

- (a) the achievement of suitable energy level schemes for laser action exemplifies basic principles of atomic and molecular spectroscopy, photochemistry, energy transfer and kinetics. **[16]**
- (b) particular properties of the laser examples chosen (such as bandwidth, high power, tunability, polarisation, coherence) can be used to study processes of interest in chemistry. **[14]**

6.

(a) A particle of mass m moves in the one-dimensional potential

$$\begin{aligned} V(x) &= 0 & -a \leq x \leq a \\ V(x) &= \infty & x > a \text{ and } x < -a \end{aligned}$$

The normalised eigenfunctions of its Hamiltonian operator \hat{H} are

$$\begin{aligned} \phi_n &= \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & n = 1, 3, 5 \dots \\ \phi_n &= \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & n = 2, 4, 6 \dots \end{aligned}$$

(i) Sketch ϕ_1 and ϕ_2 . [2]

(ii) By substituting ϕ_n into the Schrödinger equation, $\hat{H}\phi_n = \varepsilon_n\phi_n$, obtain an expression for the eigenvalues ε_n . [3]

(iii) Verify that the eigenfunctions ϕ_n are orthonormal. [3]

(b) Consider the particle in the state

$$\psi(t) = c_1(t)\phi_1 + c_2(t)\phi_2$$

where $c_1c_1^* + c_2c_2^* = 1$.

(i) Using the time-dependent Schrödinger equation

$$\frac{d\psi}{dt} = -\frac{i}{\hbar} \hat{H}\psi$$

show that

$$c_m(t) = c_m(0) \exp(-i\varepsilon_m t / \hbar)$$

where $m = 1$ or 2 . [3]

Question continues

(ii) Obtain an expression for $\psi(t)\psi(t)^*$ in terms of ϕ_1 and ϕ_2 when the initial state of the particle is defined by $c_1(0) = 1$, $c_2(0) = 0$ and comment on the result. [4]

(iii) For the initial condition $c_1(0) = c_2(0) = 1/\sqrt{2}$, show that

$$\psi(t)\psi(t)^* = \frac{1}{2}(\phi_1 + \phi_2)^2 \cos^2(\frac{1}{2}\omega t) + \frac{1}{2}(\phi_1 - \phi_2)^2 \sin^2(\frac{1}{2}\omega t) \quad [3]$$

(iv) Sketch $\phi_1 \pm \phi_2$ for $-a \leq x \leq a$. Sketch $\psi(t)\psi(t)^*$ from (b)(iii) for $t = 0$ and $t = \pi/\omega$ and comment on the result with reference to your answer to (b)(ii). [4]

(c) In an NMR experiment a collection of identical non-interacting spin- $1/2$ nuclei are subjected to a short, intense pulse of radiofrequency radiation such that they are left in the state

$$\psi(0) = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2$$

where ϕ_1 and ϕ_2 represent the $m_I = +1/2$ and $-1/2$ nuclear spin states, respectively.

Obtain an expression for the time-dependence of the integral $\langle \psi(t) | \hat{I}_x | \psi(t) \rangle$ and comment on its significance in the context of Fourier transform NMR spectroscopy. [12]

The following information may be useful.

The spin Hamiltonian (in frequency units) after the end of the pulse is $\hat{H} = \omega \hat{I}_z$.

\hat{I}_x and \hat{I}_z are spin angular momentum operators for the x and z axes.

$$\begin{aligned} \langle 1 | \hat{I}_x | 1 \rangle &= \langle 2 | \hat{I}_x | 2 \rangle = 0 \\ \langle 1 | \hat{I}_x | 2 \rangle &= \langle 2 | \hat{I}_x | 1 \rangle = \frac{1}{2} \\ \langle 1 | \hat{I}_z | 1 \rangle &= -\langle 2 | \hat{I}_z | 2 \rangle = \frac{1}{2} \\ \langle 1 | \hat{I}_z | 2 \rangle &= \langle 2 | \hat{I}_z | 1 \rangle = 0 \end{aligned}$$

Note that $|1\rangle \equiv \phi_1$, $|2\rangle \equiv \phi_2$.

Last page

Turn over