Wednesday 29 May 1996   1.30 to 4.30

CHEMISTRY A: PAPER 1

All candidates should attempt FIVE questions, with no more than TWO questions from any one section.

Linear and semi-log graph paper are available if required.

Write on ONE side of the paper only.

The answers to each question should be returned separately.

A separate cover sheet for each question should be completed.

Values of Physical Constants

$R = 8.314$ J mol^{-1} K^{-1}

$k_B = 1.3807 \times 10^{-23}$ J K^{-1}

$h = 6.6261 \times 10^{-34}$ J s

$\hbar^2/2m_e = 6.1 \times 10^{-39}$ J^2 s^2 kg^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Atomic mass unit $= 1.66053 \times 10^{-27}$ kg

$m_e = 9.10939 \times 10^{-31}$ kg

1 atmosphere $= 1.013 \times 10^5$ N m$^{-2} = 760$ Torr

$c = 2.997925 \times 10^8$ m s$^{-1} = 2.997925 \times 10^{10}$ cm s^{-1}

$F = 9.649 \times 10^4$ C mol^{-1}

$\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 J^{-1} m^{-1}

$(4\pi\varepsilon_0)^{-1} = 8.99 \times 10^9$ J m C^{-2}

$e = 1.602 \times 10^{-19}$ C

1 eV $= 8065.5$ cm$^{-1} = 1.602 \times 10^{-19}$ J

SECTION A
Quantum   Chemistry

A1
In the context of the electronic states of atoms what are ***configurations***, ***terms*** and ***levels***?

State Hund's rules for the ordering of terms and levels. Give a justification for Hund's rule as applied to the ordering of singlet and triplet terms.

What terms can arise from a $(2p^1 3d^1)$ configuration? What is the order of the levels in the term with lowest energy?

A2

The hamiltonian for the harmonic oscillator may be written

$$H = -\frac{1}{2}\frac{d^2}{dq^2} + \frac{1}{2}q^2$$

The lowest two eigenfunctions (not normalised) of this hamiltonian are

$$\Psi_0 = \exp(-\tfrac{1}{2}q^2) \quad \text{and} \quad \Psi_1 = \sqrt{2}q\exp(-\tfrac{1}{2}q^2)$$

Calculate the energies corresponding to these eigenfunctions. A term describing anharmonicity in the vibration is added to the hamiltonian to give

$$H_a = H + cq^4$$

Calculate the expectation value of H_a with Ψ_0, and with Ψ_1. Is the spacing of the vibrational levels in a real molecule greater or less than that calculated by a harmonic oscillator model, and what does this imply about the sign of the constant c in H_a?

$$\int_{-\infty}^{\infty} q^{2n}\exp(-q^2)dq = \frac{1.3.5....(2n+1)}{2^n(2n+1)}\sqrt{\pi}$$

A3

Write down the Huckel secular equations for the four π electrons in butadiene (C_4H_6, below),
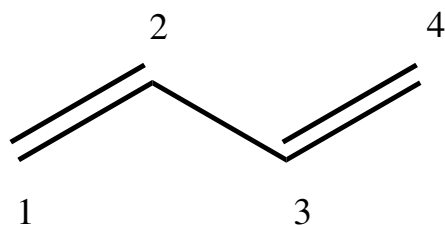
Calculate the energies of the four π molecular orbitals within the Huckel approximation. The corresponding π molecular orbital coefficients (c_1-c_4) are

Molecular orbital	c_1	c_2	c_3	c_4
1	0.3717	0.6015	0.6015	0.3717
2	0.6015	0.3717	−0.3717	−0.6015
3	0.6015	−0.3717	−0.3717	0.6015
4	−0.3717	0.6015	−0.6015	0.3717

Deduce the π electron charges on each carbon atom and the π bond orders in the ground state of butadiene. Comment on your results.

SECTION B

Spectroscopy

A4

An infrared spectrum of the fundamental band of $D^{35}Cl$ shows rotational structure in the P and R branches. Lines are seen at the following wavenumbers (in cm^{-1}):

2131.91 2122.05 2111.94 2101.60 2080.26 2069.24 2058.02 2046.58

Assign rotational quantum numbers for both $v = 0$ and $v = 1$ levels to each transition. Calculate the rotational constants in both vibrational levels ($\tilde{B}_0$ and $\tilde{B}_1$), ignoring the effect of centrifugal distortion. For both levels, calculate the bond length. Comment on your results.

Estimate the rotational constant ($\tilde{B}_2$) for the $v = 2$ level.

Atomic masses / atomic mass unit: $D = 2$ $Cl = 35$

A5

Describe the physical processes responsible for

(i) natural line broadening
(ii) Doppler broadening
(iii) pressure broadening

of spectral lines.

Explain how, when measurements are made in the microwave region of the spectrum, the pressure broadening of lines can help to provide information on the distribution of ClO with altitude in the atmosphere.

A satellite observes a planetary atmosphere by means of a microwave spectrometer measuring radiation emitted by CO gas in the planet's atmosphere. At what frequencies (in cm^{-1}) will the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ rotational transitions be measured. The ratio of the intensities of the $J = 1 \rightarrow 0$ to $J = 2 \rightarrow 1$ lines is found to be 0.635. Make a rough estimate of the temperature of the planet, mentioning any assumptions involved in your calculation.

Atomic masses / atomic mass unit $O = 16$ $C = 12$
The internuclear separation in CO is 0.1128 nm

SECTION C
Statistical Mechanics

A6

Explain what is meant by the term ***state function*** and indicate briefly why such functions are of importance in thermodynamics. State the Third Law of Thermodynamics and explain concisely how it may be understood at the microscopic level.

Consider the gaseous equilibrium

$$Na_2 \rightleftarrows 2Na$$
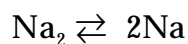
Using the following data, obtain a value for the constant volume equilibrium constant (K_c) of this reaction at 800 K.

Θ_{rot} (Na$_2$) = 0.2 K $\qquad$ q_{trans} (Na$_2$) = $\dfrac{f_{trans}(Na_2)}{V}$ = 1.325×10^{33} m^{-3}

Θ_{vib} (Na$_2$) = 100 K $\qquad$ q_{trans} (Na) = $\dfrac{f_{trans}(Na)}{V}$ = 4.685×10^{32} m^{-3}

Dissociation energy of Na$_2$ = 70 kJ mol^{-1}
V = reaction volume

A7

What do you understand by the term ***irreversible process***? Consider the expansion of a gas from a smaller volume into a larger evacuated volume. Explain concisely how the irreversibility of such a process is connected with the gas molecules having attained the most probable partitioning between the two volumes.

Consider a diatomic molecule. In what circumstances is it valid to factorise the total molecular partition function, f_{total}, according to
$f_{total} = f_{trans}.f_{rot}.f_{vib}.f_{elec}$?

The NO molecule has a doubly degenerate electronic ground state and a doubly degenerate excited electronic state lying 2.4×10^{-21} J above the ground state. The vibrational frequency of the molecule is $\nu = 5.62 \times 10^{13} \, s^{-1}$.

Evaluate the vibrational and electronic partition function of NO at 300 K and comment briefly on your results.

Given that $S = -\left(\dfrac{\partial A}{\partial T}\right)_V$ evaluate the electronic contribution to the entropy at 300 K.

Friday 31 May 1996   **1.30 to 4.30**

CHEMISTRY A: PAPER 2

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SECTION A

Advanced Quantum Mechanics, Organometallic Chemistry

A8

Define the commutator $\left[\hat{A},\hat{B}\right]$ of two operators. Show that if $\left[\hat{A},\hat{B}\right]=0$ then non-degenerate eigenfunctions of $\hat{A}$ are also eigenfunctions of $\hat{B}$.

The angular momentum operators, $\hat{l}_x, \hat{l}_y, \hat{l}_z$, obey the commutator equations (in atomic units),

$$\left[\hat{l}_x,\hat{l}_y\right]=i\hat{l}_z, \quad \left[\hat{l}_y,\hat{l}_z\right]=i\hat{l}_x, \quad \left[\hat{l}_z,\hat{l}_x\right]=i\hat{l}_y$$

From these evaluate $\left[\hat{L}^2,\hat{l}_z\right]$ where $\hat{L}^2 = \hat{l}_x\hat{l}_x + \hat{l}_y\hat{l}_y + \hat{l}_z\hat{l}_z$. What does your answer imply about the simultaneous measurement of L^2 and l_z? Also show that

$$\hat{L}^2 = \hat{l}_+\hat{l}_- + \hat{l}_z\hat{l}_z - \hat{l}_z \quad \text{where } \hat{l}_+ = \hat{l}_x + i\hat{l}_y \text{ and } \hat{l}_- = \hat{l}_x - i\hat{l}_y.$$

Do either of the operators $\hat{l}_+$ or $\hat{l}_-$ correspond to observable quantities? Give your reasoning.

A9

Discuss the non-crossing rule as it applies to the electronic states of a diatomic molecule.

By considering the secular equations for a two-level electronic system within the Huckel approximation, derive an expression for the energy difference between two states. How may this expression be used to justify the non-crossing rule? Can the potential energy curves for different electronic states of a diatomic molecule ever cross? Give your reasoning.

A10

What is meant by a fluxional molecule? How may fluxionality be investigated?

Discuss the nature of the fluxional processes which lead to the following observations.

(i) The ^{1}H NMR spectrum of $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2$ shows four separate resonances at -80°C but only two resonances at $+30^\circ$C. At still higher temperatures these two resonances coalesce.

(ii) The ^{13}C NMR spectrum of $Fe(CO)_5$ shows only one resonance even at -150°C.

(iii) The ^{1}H NMR spectrum of $Pt(PEt_3)(C_2H_4)Cl_2$ shows two resonances due to the C_2H_4 protons at low temperatures but only one at higher temperatures.

A11

Describe the nature of the bonding between an alkene and a transition metal in a mononuclear complex containing such a ligand.

What important features must transition metal complexes display to enable them to act as homogeneous catalysts in catalytic reactions involving alkenes? Give a mechanism for the catalytic reaction of C_2H_4 with H_2 and CO in the presence of $Co_2(CO)_8$ (the 'OXO' reaction). Why is the rate of this reaction decreased by a very high pressure of CO?

SECTION B
Solids and Surfaces, Organic Reactions

A12

Explain the origin of energy bands in crystalline solids. Describe briefly the band structure of an elemental semiconductor and extend this to explain semiconductivity in some crystalline binary compounds.

A high purity sample of Ge is an intrinsic semiconductor at 300 K, and the threshold for continuous optical absorption is $5.5 \times 10^{5} \, \text{m}^{-1}$. Estimate the temperature increase required to double the conductivity.

A13

In what way does the electronic structure of a solid surface differ from that of the bulk? Show how this difference can be used to explain the existence of non-ideal surface structures.

A certain element crystallizes in a simple cubic structure with lattice constant 0.33 nm. Using a simple nearest neighbour bond analysis, estimate the surface energy for ideal {100} planes of this element. The energy of vaporization of the element is 160 kJ mol^{-1}.

A14

State clearly the assumptions made in deriving the Langmuir isotherm and obtain the isotherm expression for non-dissociative adsorption. Include explicitly in your answer the temperature dependence of the Langmuir constant, b.

At 300 K, the adsorption of each of two gases, A and B, on a certain solid obeys the Langmuir isotherm. Gas A, by itself, adsorbs to a fractional coverage θ of 0.01 at pressure, P = 100 mbar, and gas B, by itself, adsorbs to θ = 0.01 at P = 10 mbar. Calculate the difference between the heats of adsorption of A and B on the solid, stating any assumptions or approximations made.

A15
Answer *all* parts.

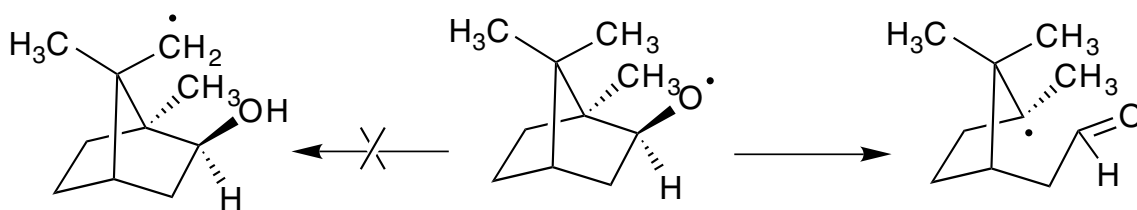(a) Draw the product of the following reaction:
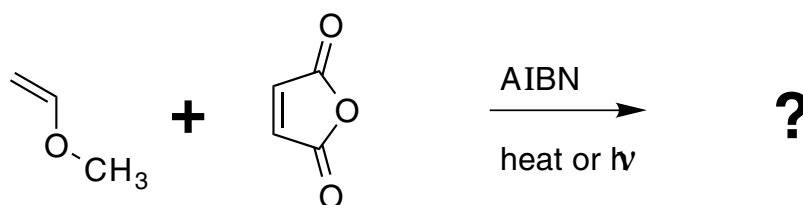
Explain the observed selectivity using Frontier Orbital Theory.

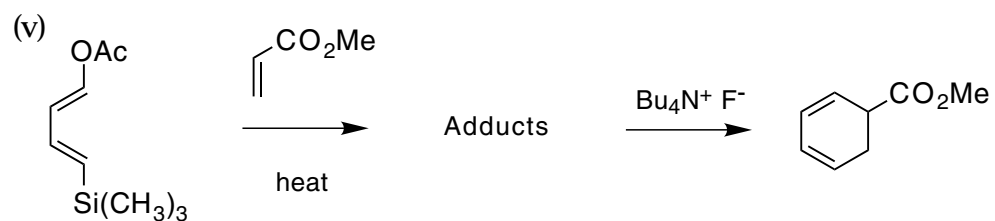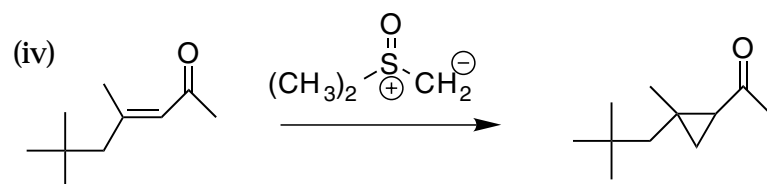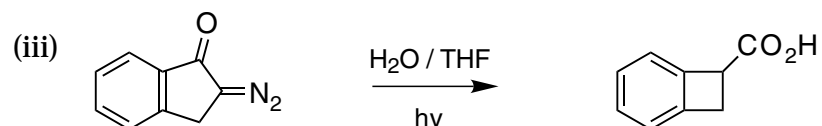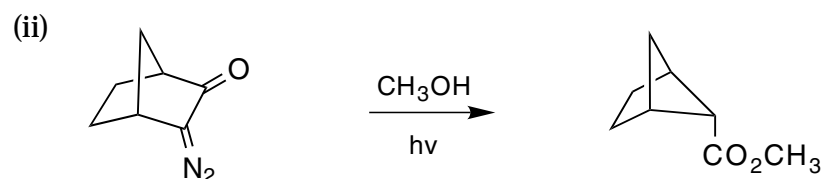(b) Rationalise the following reaction and draw the unidentified product:
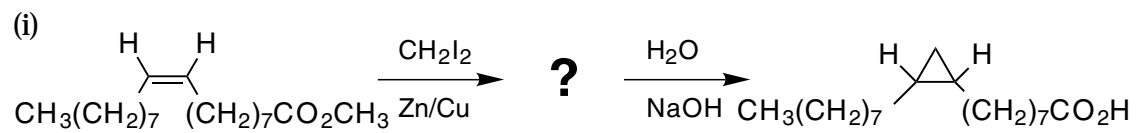

(c) Give one example of an ambident nucleophile. Explain its reactivity pattern by considering HOMO/LUMO interactions.

(d) Explain the following observation:

A16
Answer **all** parts.
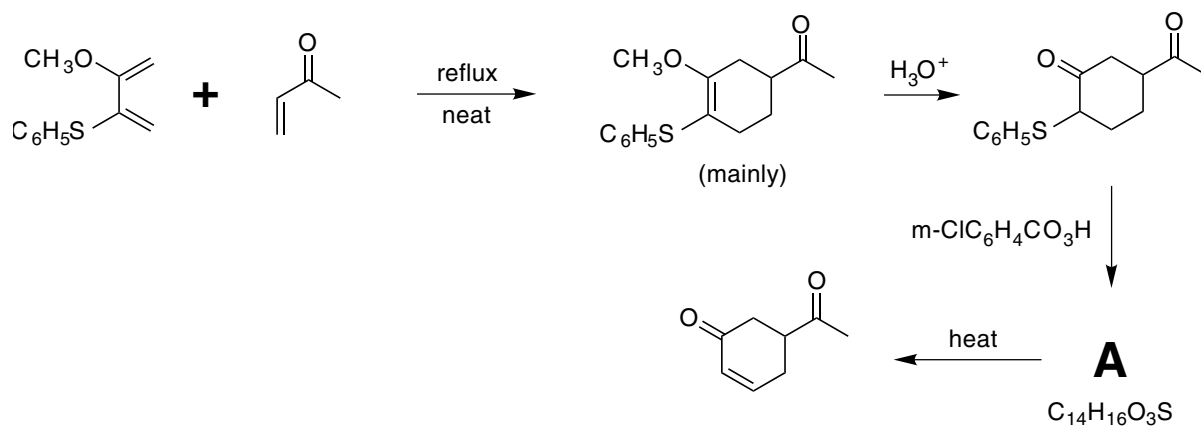
Give mechanisms for the following reactions:

(i)
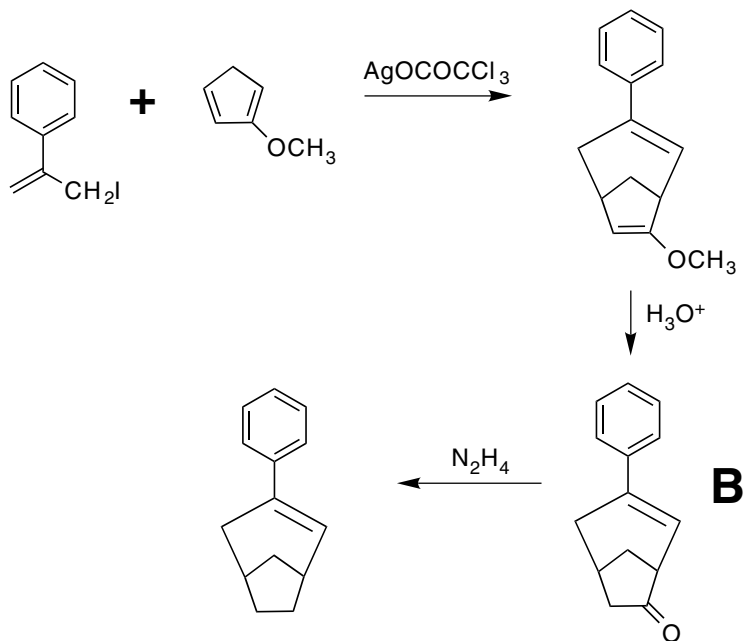

(ii)

(iii)

(iv)

(v)

A17
Answer **all** parts.

(a) Suggest a mechanism for each reaction step. Identify compound **A**.

(b) Suggest mechanisms for each reaction step.

(c) Compound **B** (see previous page) is reacted with the following reagents. Identify the products and suggest a mechanism for each reaction.

$$\textbf{B} \quad \xrightarrow[\text{2) Base}]{\text{1) Me}_3\text{SI}} \quad \textbf{?}$$

$$\textbf{B} \quad \xrightarrow[\text{2) NaH}]{\text{1) Me}_3\text{Si}\diagup\!\diagdown\text{MgCl}} \quad \textbf{?}$$
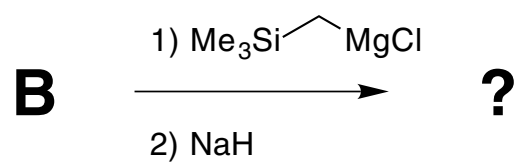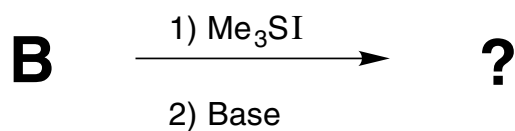
SECTION C

Reaction   Kinetics

A18

Give an account of *one* method for determining the rate of a fast reaction in solution. Describe the effect of hydrostatic pressure on the rate of a reaction in solution and derive an expression for the variation of the reaction rate constant, k_R, with pressure.

The rate constant, k_R, for the slow alkaline-catalysed hydrolysis of propionamide ($CH_3CH_2CONH_2$):

$$CH_3CH_2CONH_2 + H_2O \rightarrow CH_3CH_2COOH + NH_3 \quad (k_R)$$

was measured at T = 298 K as a function of the hydrostatic pressure, p (in atmospheres), yielding the following results:

p / atm.	1	300	600	1000
k_R / 10^{-5} dm^3 mol^{-1} s^{-1}	3.000	3.690	4.539	5.982

Show that the above data are in accord with your expression for k_R.

Determine the volume of activation, $\Delta V_0^{\ddagger}$, for the reaction.

A19

Give a short description of how transition state theory may be used to aid our understanding of bimolecular rate constants for the general atom-exchange reaction

$$A + BC \rightarrow AB + C$$
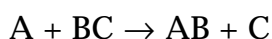
Include in your answer a description of the potential surface for the reaction and the course of the reaction in terms of motion on that surface.

The intensity, I_{em}, of the NO + O afterglow was measured in a discharge flow system containing O_2 and Ar to which a very small quantity of NO was added. The O atom concentration derived from the discharge is also very low. I_{em} is proportional to the O atom concentration. The following values for I_{em} were recorded at various positions, d, from the NO addition point along the flow for a flow velocity of 200 cm s^{-1} and where $[O_2] = 2.0 \times 10^{16}$ molecules cm^{-3} and $[Ar] = 2.0 \times 10^{17}$ atoms cm^{-3}.

d / cm	0	20	40	60
I_{em} / arb. units	100	80.3	64.4	51.7

(i) Show that atomic oxygen, O, is removed by pseudo-first-order decay and determine the first-order decay coefficient (k').

(ii) Assuming removal of atomic oxygen can be attributed solely to the third-order reaction

$$O + O_2 + Ar \rightarrow O_3 + Ar \quad (k_R)$$
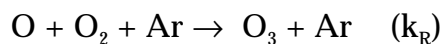
and neglecting any significant growth in the O_3 concentration, determine the third-order rate constant k_R.

SECTION D

Photochemistry and Reaction Dynamics, Bioinorganic Chemistry
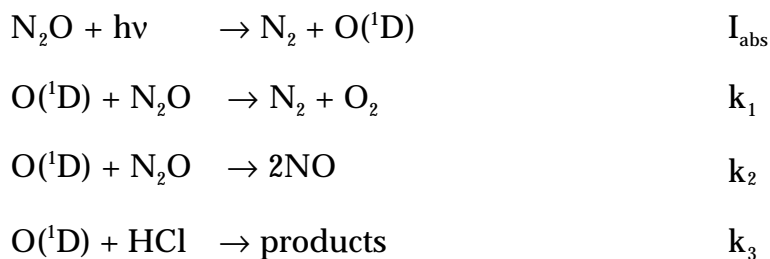
A20

Describe what you understand by the term **quantum yield** and give **one** example of how the quantum yield may be used to test the mechanism of a photochemical reaction.

The steady photolysis of N_2O at low wavelength was investigated in the presence of HCl. The quantum yield for the production of N_2, Φ_{N_2}, was measured for low degrees of photochemical decomposition using a fixed concentration of $N_2O = 5.0 \times 10^{17}$ molecules cm^{-3} and varying concentration of HCl. The following results were obtained:

$[HCl]/10^{17}$ molecules cm^{-3}	0	5.0	10.0	15.0
Φ_{N_2}	1.500	1.262	1.177	1.134

(N.B. When $[HCl]/10^{17}$ molecules cm^{-3} = 5.0 in the above table, $[HCl] = 5.0 \times 10^{17}$ molecules cm^{-3}.)

A simple mechanism may be used to describe the reaction which involves the highly reactive, electronically excited oxygen atom, $O(^1D)$, the concentration of which may be placed in steady state:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad\qquad I_{abs}$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad\qquad k_1$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad\qquad k_2$$

$$O(^1D) + HCl \rightarrow products \qquad\qquad k_3$$

(i) Write down an expression for $d[N_2]/dt$ and thus obtain an expression for Φ_{N_2} in terms of the rate constants given with the reaction equations (previous page).

(ii) Hence show that

$$\frac{1}{\Phi_{N_2} - 1} = \frac{k_1 + k_2}{k_1} + \frac{k_3[\text{HCl}]}{k_1[N_2O]}$$

(iii) Determine k_2/k_1 and k_3/k_1 from the data given.

A21

Give an account of *two* methods for studying the distribution of energy in the products from simple chemical reactions in gases.

The reaction,

$$CN + O_2 \rightarrow NCO + O \qquad\qquad (k_R)$$

was investigated at room temperature by laser-induced fluorescence (LIF) monitoring of CN via its (B-X) electronic spectrum in the region $\lambda = 420$ nm. The CN radical in its electronic ground state (X) was generated from the photolysis of a small quantity of NCNO with a separate laser in the presence of excess buffer gas and excess molecular oxygen where $[O_2] = 4 \times 10^{14}$ molecules cm^{-3}. The intensity, I_F, of the LIF spectrum of CN excited by a dye-laser (and which is proportional to the CN ground state concentration) was recorded at different times, t, yielding the following results:

t/µs	0	50	100	200
I_F/arb. units	100	60.7	36.8	13.5

      (i) Show that CN is removed by pseudo first-order decay and determine the first-order decay coefficient (k').

      (ii) Hence determine the rate constant, k_R, for the above reaction.

$(1 \ \mu s = 10^{-6} \ s)$.

A22

Answer *both* parts.

a) Why are the structures of metalloenzymes much harder to study than those of most synthetic compounds? What are the most useful experimental methods for studying the structures of metalloenzymes? What information can these techniques provide, and what are their limitations?

b) The bacterial enzyme hydrogenase, which catalyses the reversible oxidation of H_2 to protons (equation 1), is irreversibly inhibited by CN^- *via* an unknown mechanism. Hydrogenase has a nickel-containing active site, together with one or more iron/sulfur clusters (depending on the source of the enzyme). Given that both the nickel and iron sites in this enzyme are paramagnetic, what experiments would you perform in order to determine the mode of action of this inhibitor and what would each experiment tell you?

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad\qquad (1)$$

The major isotopes available are:
^{12}C: $I = 0$, natural abundance 99 %. ^{13}C: $I = 1/2$, natural abundance 1 %.
^{14}N: $I = 1$, natural abundance 99 %. ^{15}N: $I = 1/2$, natural abundance 0.4 %.
^{56}Fe: $I = 0$, natural abundance 92 %. ^{57}Fe: $I = 1/2$, natural abundance 1 %.
^{58}Ni and ^{60}Ni: $I = 0$, total natural abundance 94 %.
^{61}Ni: $I = 3/2$, natural abundance 1 %.

A23

Answer *all* parts.

a) The Fe^{3+} ion sometimes functions as a Lewis acid in the active sites of hydrolytic enzymes. Why is iron not often found in this type of metalloenzyme? Which metals are more commonly employed, and why?

b) The heme proteins, hemoglobin and cytochrome P450, bind and activate molecular oxygen in different ways. What are these different reactions? What structural differences of the heme group alter its reactivity in these two enzymes?

c) Hemocyanin is another oxygen-carrier protein, which reversibly coordinates O_2 at a dinuclear copper centre. Superoxide dismutase, which also has a dinuclear copper-containing active site, catalyses the disproportionation of $[O_2]^-$ (equation 1). What features of the metal sites in these enzymes reflect this difference in reactivity?

$$2[O_2]^- \longrightarrow [O_2]^{2-} + O_2 \qquad\qquad (1)$$
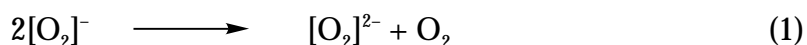
d) Why is cyanide poisonous to animals?