

SECOND PUBLIC EXAMINATION

Honour School of Chemistry

CHEMISTRY PART IB

OPTIONS PAPER

SAMPLE 2012

(3 hrs)

Candidates should answer **THREE** questions.

The numbers in square brackets indicate the approximate marks that the examiners intend to assign to each part of the question. The content represents the styles of question that are likely in these options. Note that the course content in each year may change so these sample questions are not supposed to take the place of the syllabus.

Guide to questions

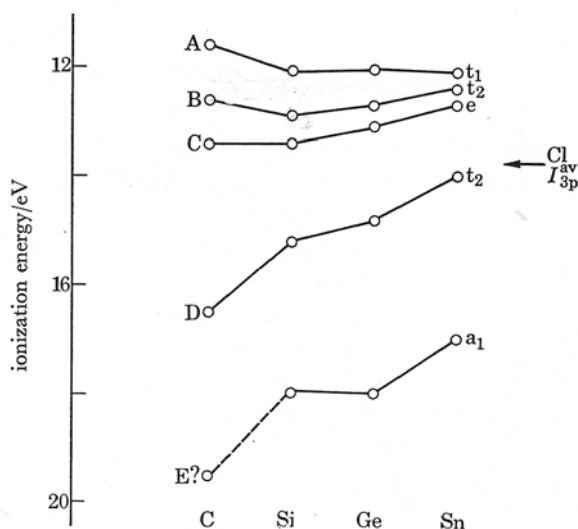
1	Inorganic molecular spectroscopy	p 2	9	Advanced synthesis and total synthesis	p 23
2	Structural methods	p 6	10	Advanced chemical biology	p 25
3	Organometallic chemistry. Structure, bonding and catalysis	p 8	11	Fundamentals of Atmospheric and Astrochemistry	p 27
4	Supramolecular, nano and medicinal inorganic chemistry	p 12	12	Molecular reaction dynamics	p 30
5	Solid state compounds in technology	p 14	13	Biophysical chemistry	p 32
6	Natural product chemistry	p 16	14	Theoretical chemistry	p 36
7	Functional organic polymers and materials chemistry	p 18	15	Advanced structural, scattering and surface methods	p 38
8	Contemporary methods in Catalysis for Organic Synthesis	p 20	16	Magnetic resonance	p 40

1. Molecular spectroscopies

Answer **ANY TWO** of Parts A–D

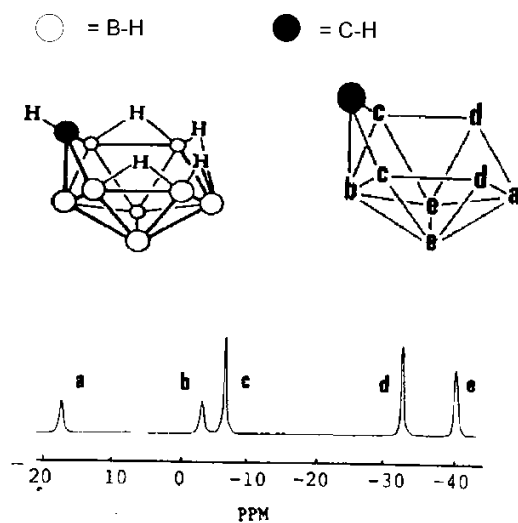
A. Answer **BOTH** parts (a) & (b)

- (a) Show that the chlorine $3p(\sigma)$ orbitals in CCl_4 transform as $a_1 + t_2$ and that the chlorine $3p(\pi)$ orbitals transform as $e + t_2 + t_1$. Hence construct a schematic MO diagram for CCl_4 and predict the qualitative appearance of the photoelectron spectrum of CCl_4 . [9]
- (b) Discuss the trends revealed by the binding energies for the valence orbitals of the chlorides $\text{CCl}_4 - \text{SnCl}_4$ derived from the photoelectron spectra, as shown below. (Bands due to ionisation of Cl $3s$ orbitals are not observed). [6]



B. Answer **BOTH** parts (a) & (b)

- (a) The acronyms COSY and NOESY stand for Correlated Spectroscopy and Nuclear Overhauser Effect Spectroscopy, respectively. Briefly explain the underlying principles of two-dimensional NMR in general and discuss how COSY and NOESY help in structure analysis of chemical compounds – devote particular attention to discussing the measurements of through bond and through space interactions. [8]
- (b) The figure below shows a carborane, B_8CH_{14} . Predict the appearance of the corresponding proton-decoupled $\{^1\text{H}\}^{11}\text{B}$ two-dimensional COSY spectrum given the one-dimensional ^{11}B spectrum below and account for the structure. [7]



C. Answer All Parts (a) – (d)

The dioxo-osmium(VI) ion $[\text{Os}(\text{O})_2\text{Cl}_4]^{2-}$ shows the following bands in the infrared and Raman spectra:

Raman (cm^{-1})	Infrared (cm^{-1})
808 * (P)	837*
375 (P)	325
302	308*
201	234
184	168

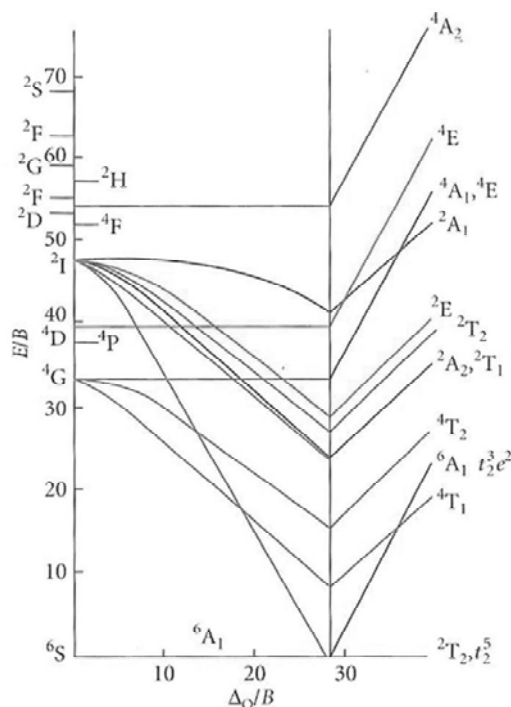
P: Polarised Raman band. *: These bands shift significantly on ^{18}O substitution. In addition a fundamental mode at 120 cm^{-1} was deduced from analysis of the overtone and combination bands.

- (a) Show that the 11 fundamental frequencies of vibration and the infrared and Raman activities are consistent with D_{4h} symmetry for the complex ion [8]
- (b) Assess qualitatively and sketch the displacements associated with the normal modes of vibration of the $\text{Os}(\text{O})_2$ fragment and assign these to the observed bands. [2]
- (c) Assess and sketch the stretching normal modes of the OsCl_4 fragment in the ion and assign these to the observed bands. [3]

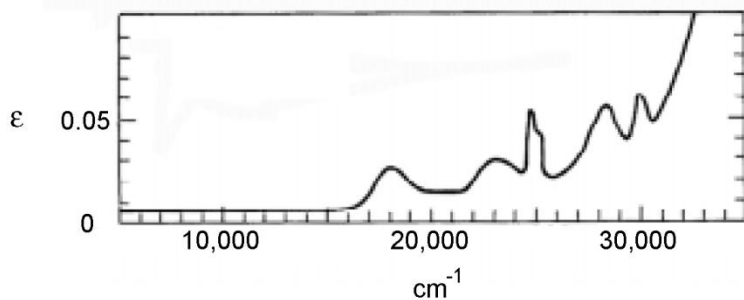
- (d) By considering the splitting pattern of the 5d orbitals of Os, paying special attention to the p-interactions between Os and O, suggest reasons why this d^2 complex is diamagnetic. [2]

D. Answer Both Parts (a) and (b)

- (a) Discuss the value and limitations of a Tanabe-Sugano diagram in the analysis of transition metal electronic spectra, with reference to the diagram for the d^5 configuration shown below. In particular, use this diagram to estimate the value of $10Dq$ (Δ) for the $Mn^{2+}(aq)$ ion using the spectrum shown. [8]



Tanabe-Sugano diagram for d^5 ion; $C/B = 4.48$



(b) Comment on the data in the table that show the position of the sharp bands (given in cm^{-1}) that correspond to that located near 25000 cm^{-1} in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. [7]

$\text{Mn}^{2+}(\text{g})$	26846
$\text{MnF}_2(\text{s})$	25300
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	25000
$\text{Mn}(\text{H}_2\text{O})_4\text{Cl}_2$	24659
$[\text{Mn}(\text{EDTA})]^{2-}$	24000
$[\text{Mn}(\text{en})_3]^{2+}$	23800
$\text{MnO}(\text{s})$	23800
$[\text{MnBr}_4]^{2-}$	22300
$\text{MnS}(\text{s})$	21600

2. Structural methods

Answer Part A AND Part B.

A Write a short essay on *ONE* of the following (a) – (c) [15]

- (a) Compare and contrast the techniques of single crystal and powder X-ray diffraction for determining structural information. How might their relative importance change in the future?
- (b) Discuss the advantages and disadvantages of neutron diffraction methods compared with X-ray diffraction methods for determining the structures and properties of solids.
- (c) Describe techniques for investigating structures which do not show long range translational order.

B Answer *ALL* parts (a) – (c)

At 320 K strontium nickel phosphide, SrNi_2P_2 , adopts the common tetragonal ThCr_2Si_2 structure type in which the c/a ratio is typically 2.7. Atoms lie at the following locations:

Sr	0 0 0		$\frac{1}{2} \frac{1}{2} \frac{1}{2}$	
Ni	$0 \frac{1}{2} \frac{1}{4}$	$\frac{1}{2} 0 \frac{1}{4}$	$\frac{1}{2} 0 \frac{3}{4}$	$0 \frac{1}{2} \frac{3}{4}$
P	$0 0 z$	$0 0 -z$	$\frac{1}{2} \frac{1}{2} \frac{1}{2}+z$	$\frac{1}{2} \frac{1}{2} \frac{1}{2}-z$

where z lies in the range $\frac{1}{3} < z < \frac{3}{8}$

The X-ray powder diffraction pattern of SrNi_2P_2 measured at 320 K has lines with the following d -spacings in Å ($1 \text{ Å} = 10^{-10} \text{ m} = 100 \text{ pm}$).

$d / \text{Å}$	$1/d^2 / \text{Å}^{-2}$	$d / \text{Å}$	$1/d^2 / \text{Å}^{-2}$
5.3385	0.0351	1.7795	0.3158
3.7030	0.0729	1.7419	0.3296
2.7917	0.1283	1.5871	0.3970
2.6693	0.1404	1.5817	0.3997
2.6435	0.1431	1.5006	0.4441
2.4738	0.1634	1.4228	0.4940
1.9740	0.2566	1.3958	0.5133
1.9293	0.2687	1.3607	0.5401
1.8783	0.2835	1.3504	0.5483
1.8515	0.2917	1.3346	0.5614

- (a) Given the atomic coordinates and $c/a = 2.7$, explain why you expect the first line in the diffraction pattern to be the 0 0 2 reflection and the third line to be the 1 1 0 reflection. [2]
- (b) Hence index the diffraction pattern and determine the unit cell constants a and c , verifying that the volume of the unit cell is 166.5 \AA^3 . [7]
- (c) The structure factor of a 0 0 l reflection may be expressed in the form:

$$F_{00l} = 2f_{Sr} + 4f_{Ni} \cos \pi(l/2) + 4f_P \cos 2\pi lz$$

where f_{Sr} , f_{Ni} , and f_P are the atomic scattering amplitudes for the atoms.

Given that z lies in the range $1/3 < z < 3/8$ and given that the atomic scattering amplitudes appropriate to the 0 0 6 reflection are $f_{Sr} = 26.40$; $f_{Ni} = 19.47$; $f_P = 8.87$, use the fact that the 0 0 6 reflection has almost zero intensity to estimate a value for z . [6]

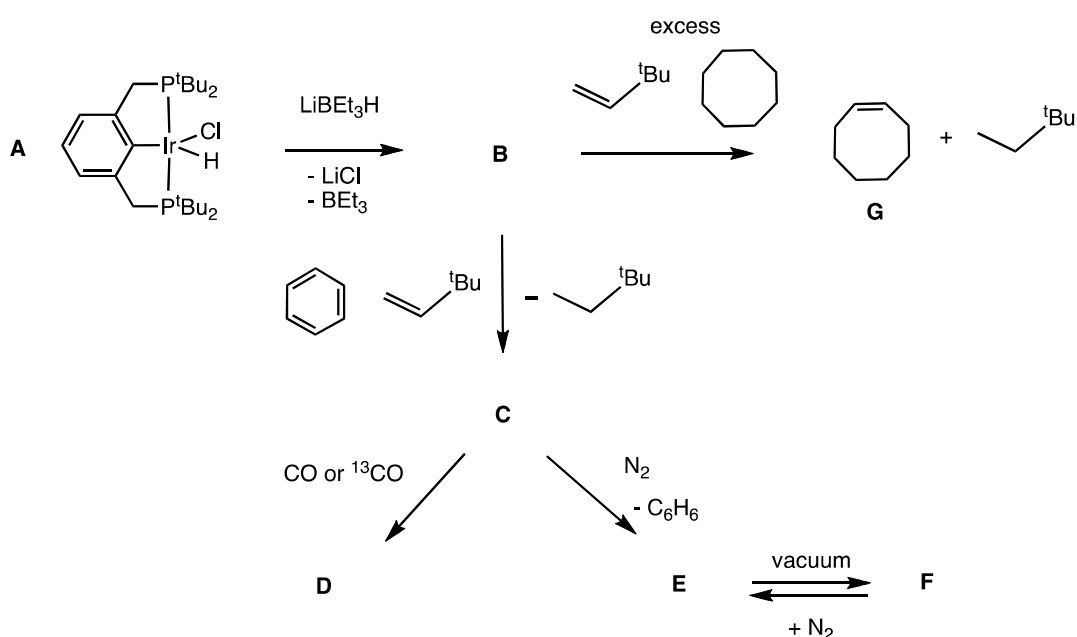
Note that for the tetragonal system: $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$

3. Organometallic Chemistry. Structure, Bonding and Catalysis

Answer *TWO* of the following Parts A–D.

A. C–H Activation

Identify and draw the structures of the complexes **B** to **F** shown below, making use of, and providing full comment upon, the selected characterisation data provided. For each reaction step provide a mechanistic rationale for the observed products. In addition, draw a mechanism for the use of **B** as a catalyst to form **G**. [15]



Selected NMR and vibrational spectroscopic characterisation data for the complexes A-F:

- A** ¹H: δ – 43.0, 1 H, t, *J* 12 Hz; ³¹P{¹H}: δ 68 (s)
- B** ¹H: δ – 9.0, 2 H, t, *J* 10 Hz; ³¹P{¹H}: δ 73 (s); *m/z* = 587.2
- C** ¹H: δ – 45.4, 1 H, t, *J* 14 Hz; ³¹P: δ 72 d, *J* = 14; *m/z* = 663.2
- D** **With CO:** ¹H: δ – 9.1, 1 H, t, *J* = 18 Hz; ³¹P: δ 53, d, *J* = 18 Hz
With ¹³CO: ¹H: δ – 8.7, 1 H, dt, *J* = 44, 18 Hz; ³¹P: δ 53, dd, *J* = 18, 6 Hz
Infra red (with CO): ν(CO): 1973 cm⁻¹
- E** ¹H: featureless hydride region, ³¹P{¹H}: δ 73
Infra red: Strong stretching bands at 2080 cm⁻¹; **Raman:** strong stretch at 2080 cm⁻¹
 In the solid-state structure there is a N-N distance of 1.10 Å

- F ^1H : featureless hydride region, $^{31}\text{P}\{^1\text{H}\}$: δ 75
Infra red: featureless between 2200 – 1880 cm^{-1} . **Raman**: strong stretch at 1979 cm^{-1}
 In the solid-state structure there is a N-N distance of 1.13 Å
 Molecular weight measurements indicate that **F** is *approximately* twice the M_w of **E**
 Atomic masses: Ir: 192.2 ; P: 31.0 ; C: 12.0
 ^1H : $I = \frac{1}{2}$, 100%; ^{31}P : $I = \frac{1}{2}$, 100%; ignore the coupling associated with the isotopes of Ir.
 $\nu(\text{N-N})$ for $\text{N}_2(\text{g})$: 2330 cm^{-1}

B. Structure and Bonding

Answer EITHER part (a) OR part (b)

- (a) Discuss the structure and bonding in “sandwich” complexes containing η -cyclopentadienyl and η -arene ligands such as ferrocene and bis(benzene)chromium. [15]
- (b) Answer ALL parts (i) – (iii)

(i) Based on the metal-carbon distances in the table, assign the letters A-D to the metallocene compounds $\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2$, $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)_2$, $\text{Mn}(\eta^5\text{-C}_5\text{Me}_5)_2$ and $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ [5]

Compound	A	B	C	D
$r_{\text{M-C}}$ / pm	206	211	228	238

(ii) Comment on the following magnetic moments (μ_{eff} / μ_B). [5]

$\text{V}(\eta^6\text{-C}_6\text{H}_6)_2$	$\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$	$\text{Fe}(\eta^6\text{-C}_6\text{H}_6)_2$
1.68	0	3.00

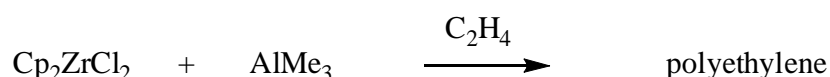
(iii) Stating your reasons clearly, place the following four compounds in order of increasing first ionisation energy. [5]

$\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$	$\text{Cr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)_2$
$\text{Mn}(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)$	$\text{Fe}(\eta^6\text{-C}_5\text{H}_5)_2$

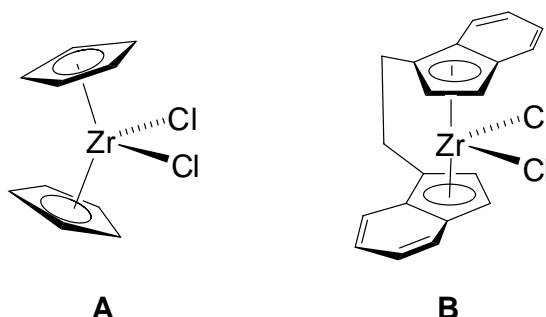
C. Polymerisation

Explain **ALL** of the following observations (a) – (d).

- (a) Introduction of trace amounts of water into the system outlined below dramatically increases the activity with respect to ethylene polymerisation. Addition of a Lewis base such as pyridine or tetrahydrofuran leads to a significant decrease in polymerisation activity. [3]



- (b) When activated with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of ethylene (5 atmosphere pressure) a toluene solution of a transition metal polymerisation precatalyst $(\text{L})\text{TiMe}_2$ (where L represents the other ligands) produced high molecular weight polyethylene. After the reaction mixture was quenched with H_3O^+ , analysis of the polymer produced showed that *ca.* 2000 chains of linear polyethylene were formed per precatalyst metal centre, and that each chain was terminated by one methyl group and one vinyl ($-\text{CH}=\text{CH}_2$) group. When the same polymerisation experiment was conducted in the presence of either a large excess of AlMe_3 or a partial pressure of H_2 , polyethylene with a lower average molecular weight was formed. Analysis of this polymer showed that fewer than 10% of the polymer chains were terminated by a vinyl group. [6]
- (c) The precatalyst **A** shown below forms predominantly atactic polypropylene when treated with a suitable activator in the presence of propylene. In contrast, precatalyst **B** forms predominantly isotactic polypropylene.



[6]

D. E–H Complexes and Functionalisation of Main Group Complexes.

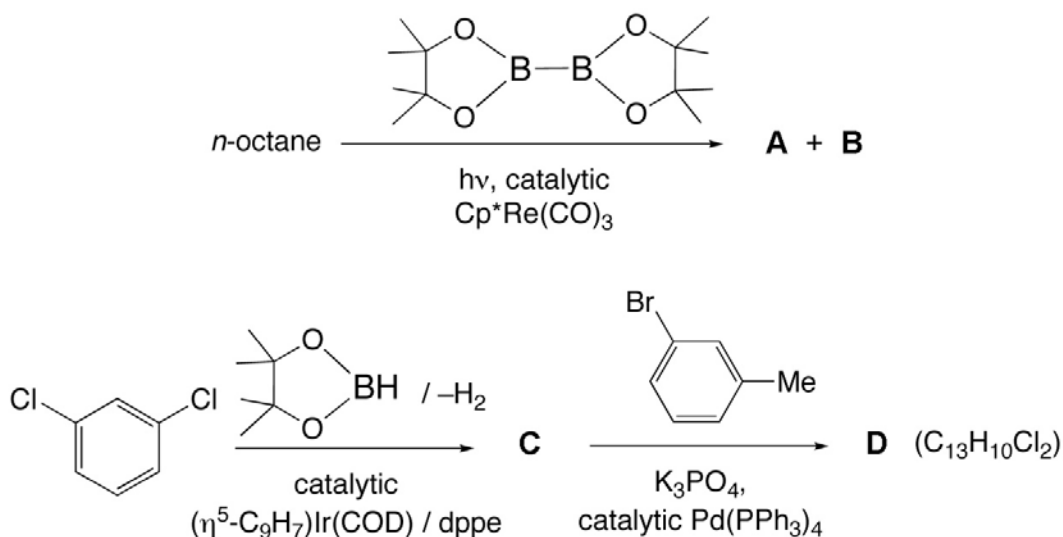
Answer both parts (a) and (b)

- (a) Rationalise, based on an appropriate bonding model, the following two sets of data relating to silane sigma complexes and related compounds: [19]

Compound	$d(\text{Mn-Si}) / \text{Å}$
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiHPh}_2)$	2.391
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiFPh}_2)$	2.352
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiPh}_3)$	2.424

Compound	$ J_{\text{Si-H}} / \text{Hz}$	$d(\text{Si-H}) / \text{Å}$	$d(\text{Mn-H}) / \text{Å}$	$d(\text{Mn-Si}) / \text{Å}$
HSiCl_3	338	1.478	-	-
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiCl}_3)$	38	1.823	1.578	2.320
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})(\text{PMe}_3)(\text{HSiCl}_3)$	22	1.833	1.580	2.288
$(\text{OC})_4\text{Fe}(\text{H})(\text{SiCl}_3)$	16	-	-	-

- (b) Identify each of the products **A–D** from the following reactions: [2 × 3]



4. **Supramolecular, Nano and Medicinal Inorganic Chemistry**

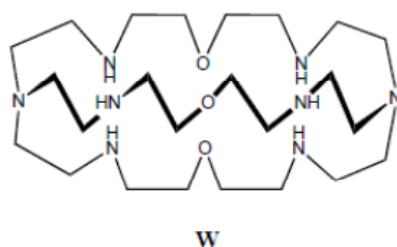
Answer BOTH part A AND Part B

A. Write an account of *one* the following: [16]

- (a) The design of ligands for complexing anionic guest species
- (b) The concept of ion-pair recognition
- (c) The factors influencing the relaxivity of gadolinium containing contrast agents
- (d) The pathways for sensitised emission in lanthanide complexes bearing an aryl chromophore
- (e) The use of radioisotopes in tomographic imaging"

B. Answer *TWO* of parts (a) – (c).

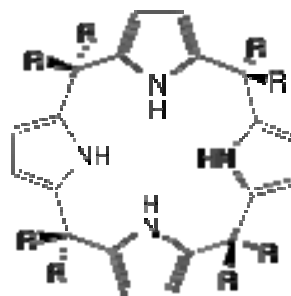
- (a) Comment on the stability constants ($\log K$) between the hexa-protonated form of ligand **W** and different anions. [7]



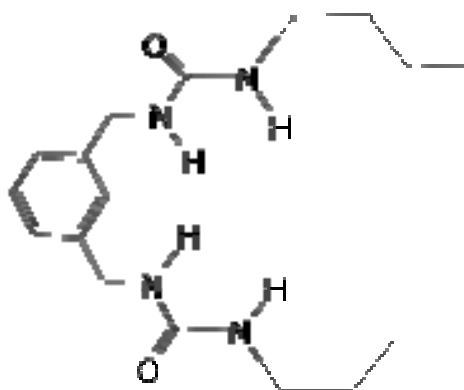
Anion	Cl	Br ⁻	N ₃ ⁻	NO ₃ ⁻	HCO ₃
log K	3.0	2.6	4.3	2.8	2.3

- (b) Discuss the following anion association constant data. (Include a brief comment on the expected relationship between receptor pK_a and $\log K$.) [7]

Anion	$\log K$
F^-	4.2
Cl^-	2.5
Br^-	1
I^-	<1
$H_2PO_4^-$	2.0
HSO_4^-	<1



- (c) Comment on the stability constant data for anionic complexes of the amide host below. [7]



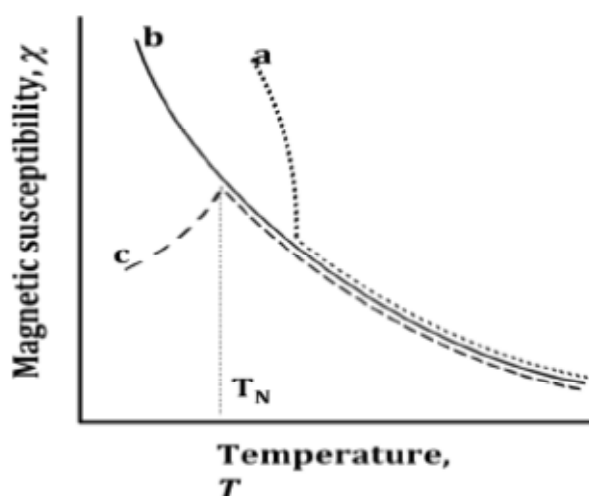
Anion	$H_2PO_4^-$	CH_3COO^-	Cl^-	HSO_4^-	NO_3^-	ClO_4^-
$\log K$ in DMSO	2.08	1.63	0.6	0	<0	No binding

5. Solid State Compounds in Technology

Answer *TWO* of Parts A-D

A. Answer *BOTH* Parts (a) and (b)

The graph below shows in schematic form the temperature dependence of the magnetic susceptibilities of paramagnetic, ferromagnetic and antiferromagnetic substances.



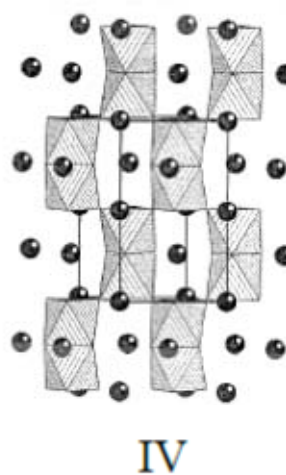
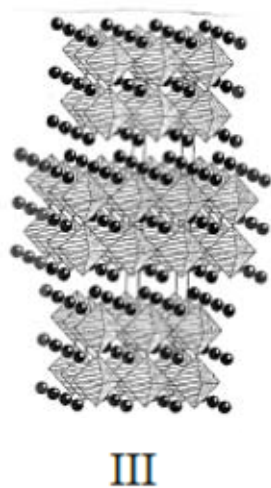
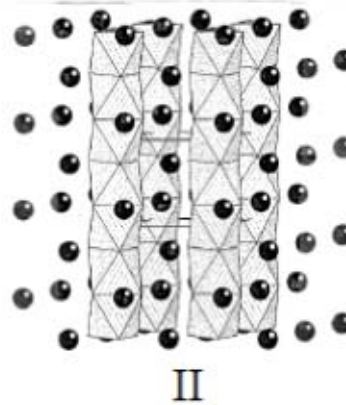
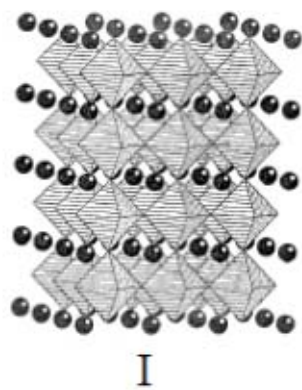
- (a) Assign each of the lines **a**, **b** & **c** to the appropriate class of substance and explain the reasons for these observed differences in temperature dependence. [7]
- (b) Using several examples discuss how antiferromagnetism and ferromagnetism may arise in solids. [8]
- B. Give an account of the growth and applications of thin films of inorganic semiconductors by metallo-organic beam epitaxy chemical vapour deposition (MOCVD) technique. Describe the concept of bandgap engineering of inorganic heterostructure semiconductors. [15]

C. Answer BOTH Parts (a) and (b)

(a) Describe the phenomenon of superconductivity discuss the factors that are important for the realisation of devices based on superconductors. [7]

(b) Give a brief account of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity and discuss, with examples, the extent to which this theory can account for the behaviour of various classes of superconducting compound [8]

D. With reference to some of following structures (I – IV), describe systematic structural variations based on perovskite and perovskite-related compounds including Ruddlesden-Popper phases. Give some potential applications of these structures. [15]

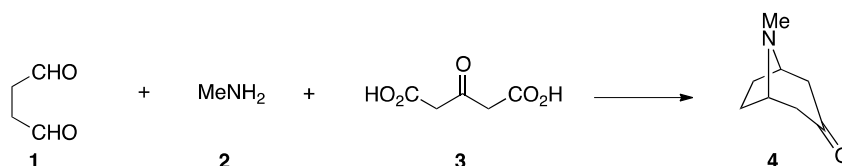


6. Natural Product Chemistry

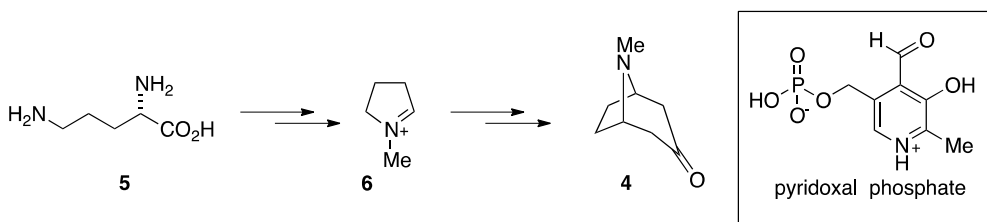
Answer *all* Parts A, B and C of this question.

Part A

Tropinone 4 can be made synthetically by combining succinaldehyde 1, methylamine 2 and acetone dicarboxylic acid 3, at pH 7. Provide a mechanism for this reaction. [4]



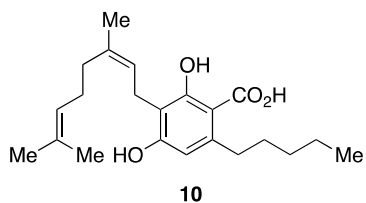
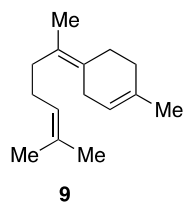
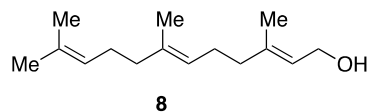
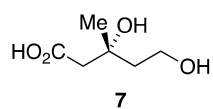
Tropinone 4 is biosynthesised from L-ornithine 5 *via* the iminium ion 6. Provide a plausible biosynthetic mechanism for the formation of 6 which uses the co-factor pyridoxal phosphate, and a plausible biosynthesis for the formation of tropinone 4 from 6. [2 × 3]



Part B

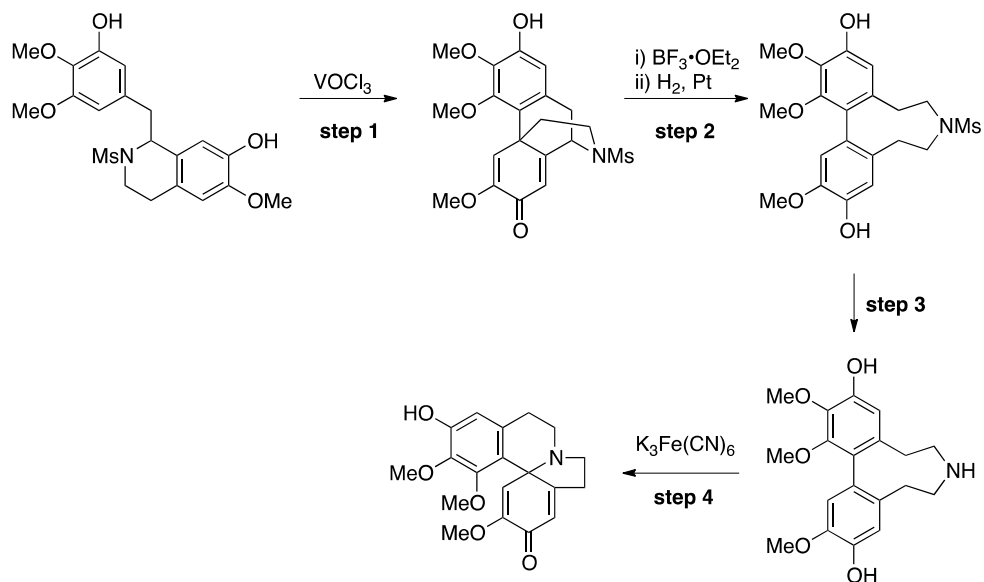
- Outline how mevalonic acid 7 is derived biosynthetically from acetic acid. [4]
- Outline how mevalonic 7 acid is metabolised to farnesol 8. [3]
- Propose outline schemes of the biosynthetic origin of the sesquiterpene bisabolene 9. [3]
- Starting from $[^{13}\text{C}]$ -labelled acetic acid ($\text{CH}_3^{13}\text{CO}_2\text{H}$) predict the labelling pattern found in cannabigerolic acid 10. [6]

QUESTION CONTINUES



Part C

A biomimetic synthesis of an erythrina alkaloid is shown below. Propose mechanisms for steps 1, 2 and 4. [8]



QUESTION ENDS

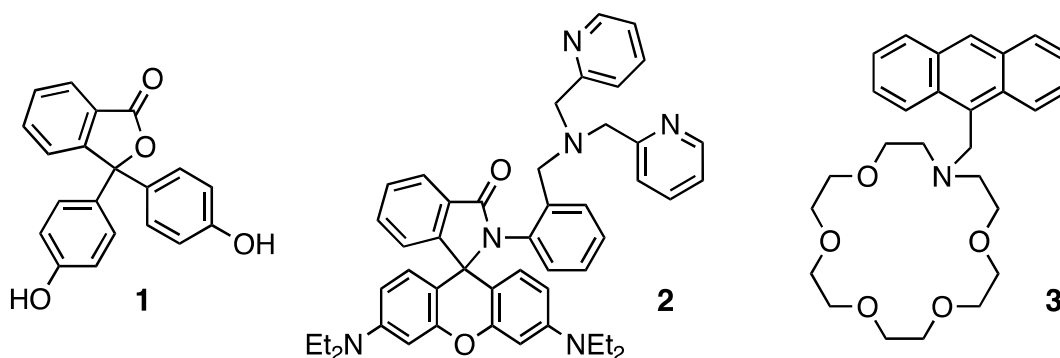
7. Functional organic polymers and materials chemistry

Answer *both* sections A and B of this question.

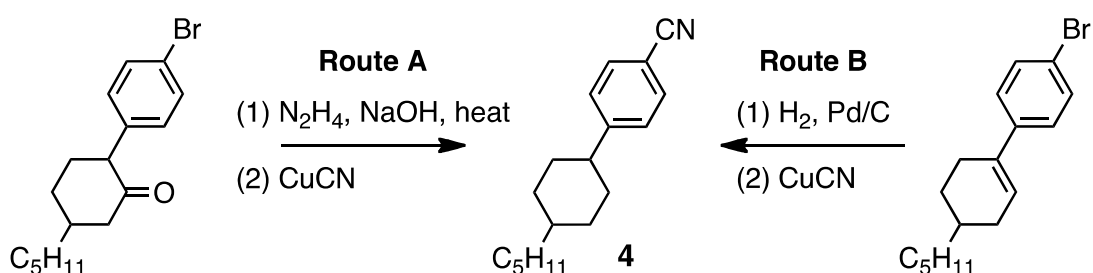
Part A.

Explain five of the following observations:

[5 × 4]

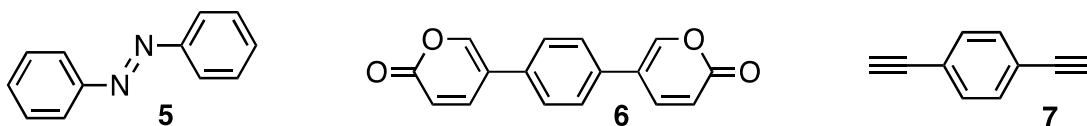


- (a) Phenolphthalein 1 becomes red under basic conditions, but is colourless at pH > 12.
- (b) Solutions of compound 2 become fluorescent in the presence of Zn²⁺ ions.
- (c) Compound 3 is weakly fluorescent in solution. It becomes more fluorescent in the presence of K⁺ ions.
- (d) Two routes to compound 4 are shown below. The product from Route A is a nematic liquid crystal whereas the product from Route B exhibits no liquid crystal phases.



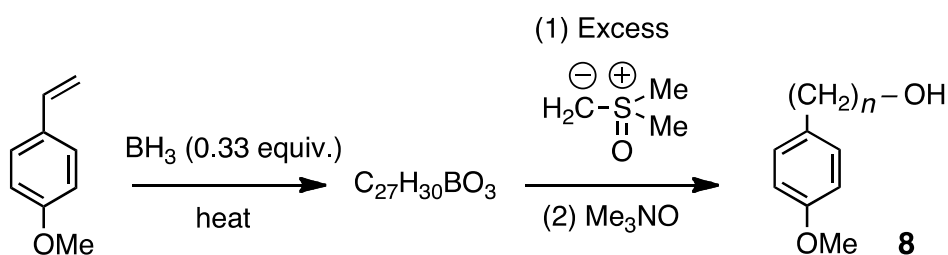
QUESTION CONTINUES

- (e) Azobenzene 5 is a photochromic dye. It is not significantly fluorescent.
- (f) When monomers 6 and 7 are heated together, they react to form poly-*para*-phenylene.

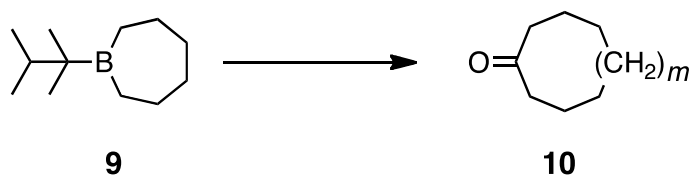


Part B.

- (a) Explain the advantages of “living” polymerisation reactions, in comparison to less controlled polymerisations. Illustrate your answer with one example of a living polymerisation reaction, including a mechanism for the reaction that you choose. [6]
- (b) The following reaction can be used to synthesise end-functionalised polyethylene 8. Suggest mechanisms for each stage in the synthesis and explain what factors determine the average degree of polymerisation, \bar{n} . [4]



- (c) Suggest how similar chemistry to that above could be used to prepare the ring polymer 10 from borane 9. (More than one step is required.) [3]



QUESTION ENDS

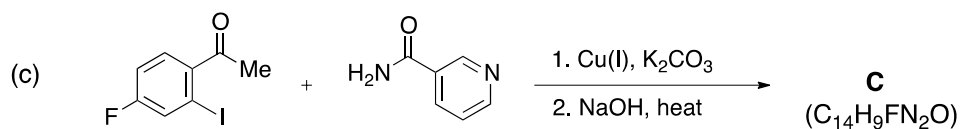
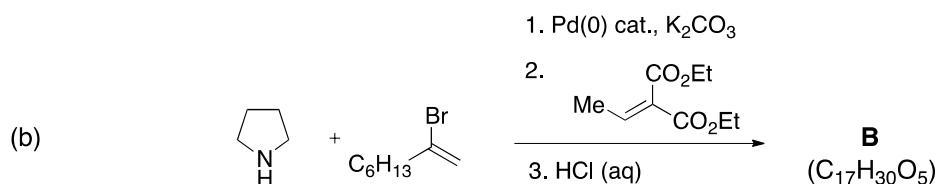
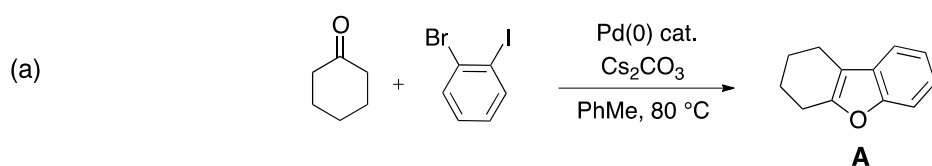
8. Contemporary methods in Catalysis for Organic Synthesis

Answer *three* Parts from Parts A, B, C and D of this question.

Part A.

[11]

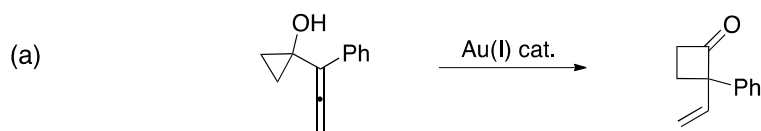
Propose intermediates, and mechanisms for all of the following transformations, and identify the products in (b) and (c).



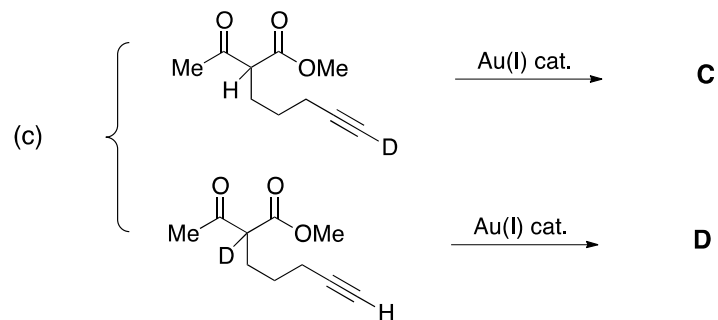
Part B.

[11]

Propose intermediates, and mechanisms for all of the following transformations, and identify the products in (b) and (c).



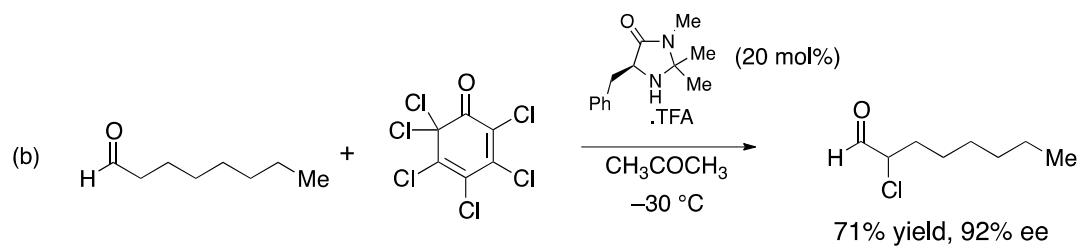
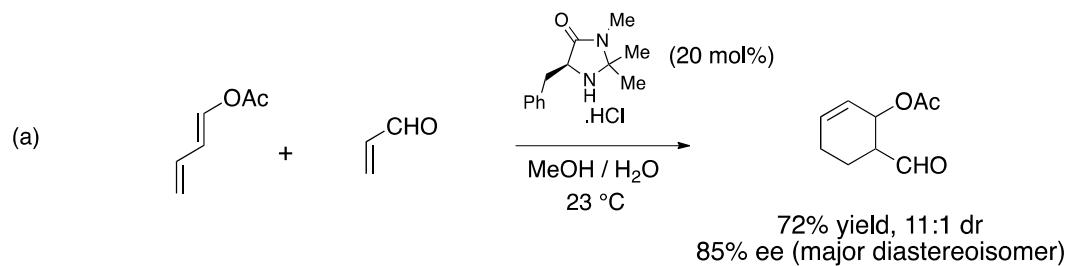
QUESTION CONTINUES



Part C.

[11]

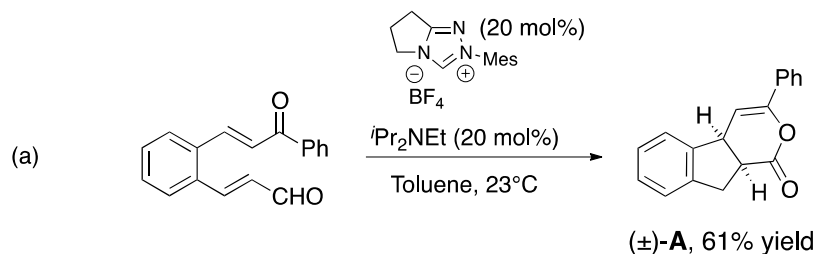
Provide mechanisms to account for the formation of the products in (a) and (b). In each case predict with reasoning the major stereoisomer.



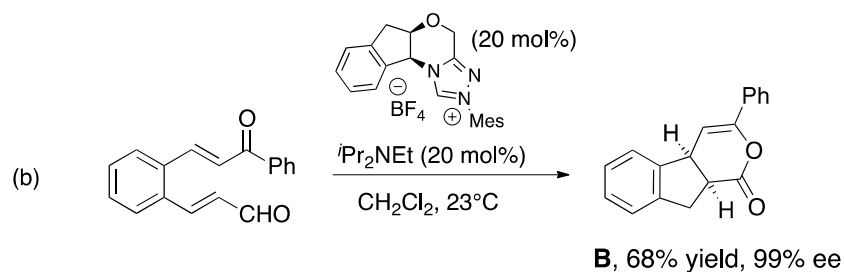
QUESTION CONTINUES

Part D.

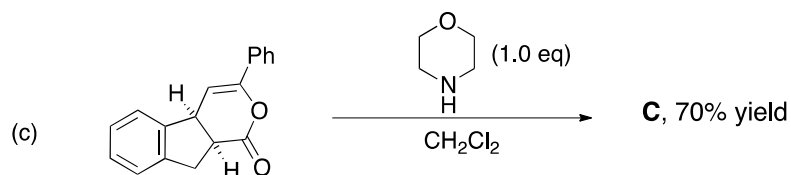
- (a) Provide a mechanism for the transformation in (a). Your answer should account for the relative stereochemistry of product A. [12]



- (b) Account for the absolute stereochemistry of product B. [5]



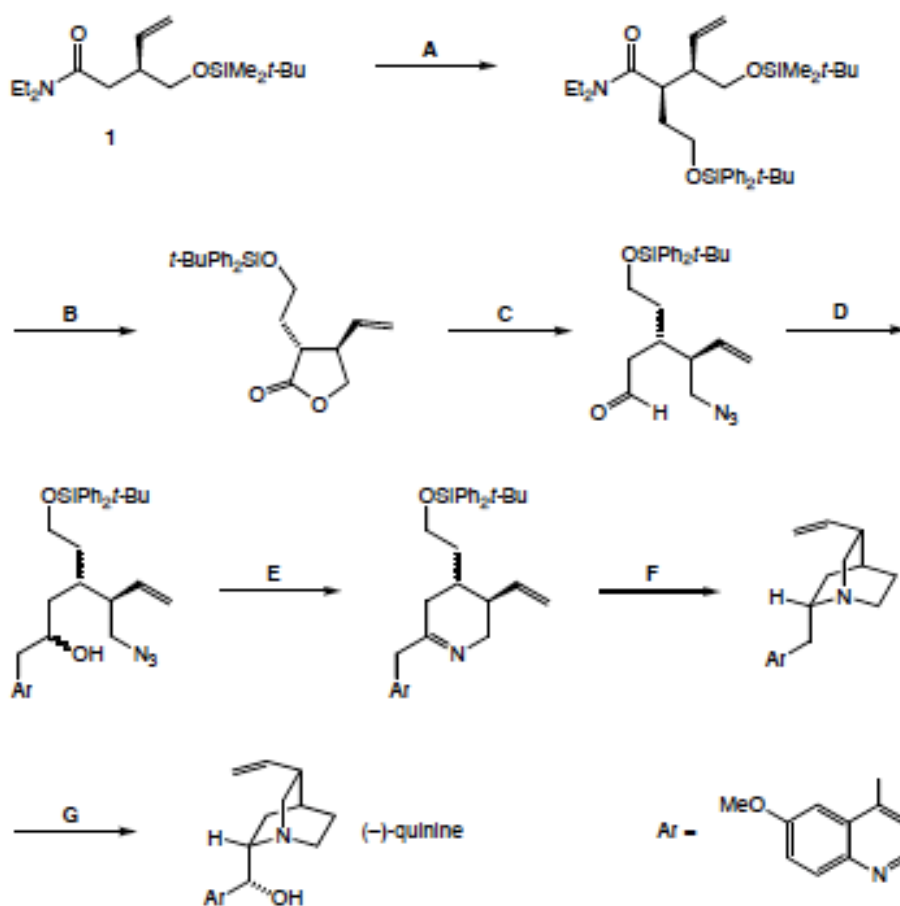
- (c) Predict product C, and provide a mechanism for its formation. [3]



QUESTION ENDS

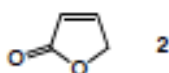
9. Advanced Synthesis and Total Synthesis

Answer all parts of this question that concerns a recent total synthesis of (–)-quinine, a historically important antimalarial plant alkaloid and ingredient of tonic water.



Note: you are *not* required to comment on transformation **D**.

- (a) Suggest a synthesis of amide **1** (as the racemate) from lactone **2**. [6]



- (b) Explain the stereochemical outcome in reaction **A** for which the reagents are: $\text{LiN}(i\text{-Pr})_2$, then $\text{ICH}_2\text{CH}_2\text{OSiPh}_2t\text{-Bu}$. [4]

QUESTION CONTINUES

- (c) Give a mechanism for reaction B for which the reagents are: cat H^+ , EtOH. Comment on the selectivity in this step. [3]
- (d) Suggest suitable reagents for transformation C (more than one step will be necessary). [8]
- (e) The reagents for transformation E are: (i) DMSO, $(COCl)_2$ then Et_3N ; (ii) Ph_3P , heat. Give plausible mechanisms for these reactions. [5]
- (f) The reagents for transformation F are: (i) $NaBH_4$; (ii) HF; (iii) CH_3SO_2Cl , heat. Explain the stereoselectivity in step (i) of this sequence and give mechanisms for steps (ii) and (iii). [5]
- (g) Suggest plausible reagents to achieve the oxidation reaction G. You are *not* required to address the stereochemistry in this step. [3]

QUESTION ENDS

10. Advanced Chemical Biology

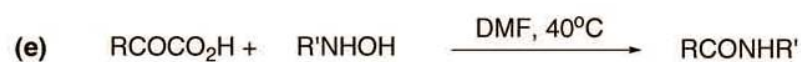
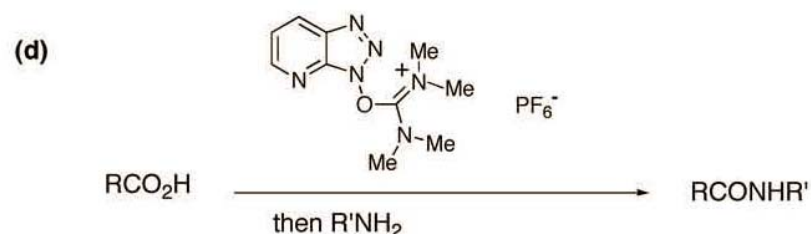
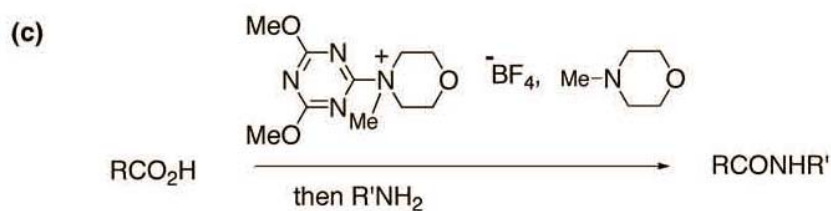
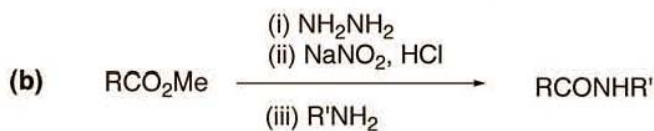
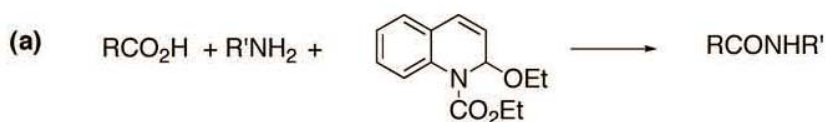
Answer all parts A, B and C

Part A

- (i) What is the key bond-forming event that the ribosome catalyses and what is the molecular mechanism of this catalysis? You may use abbreviated versions of the catalytic site with truncated forms of ribosomal residues for simplicity. [4]
- (ii) This bond-forming event that the ribosome catalyses may be catalysed by other biomolecules. Give an example that illustrates an alternative catalytic mechanism. [5]

Part B

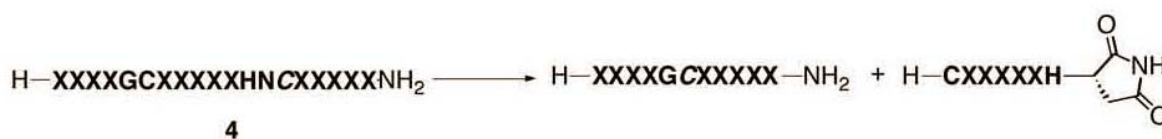
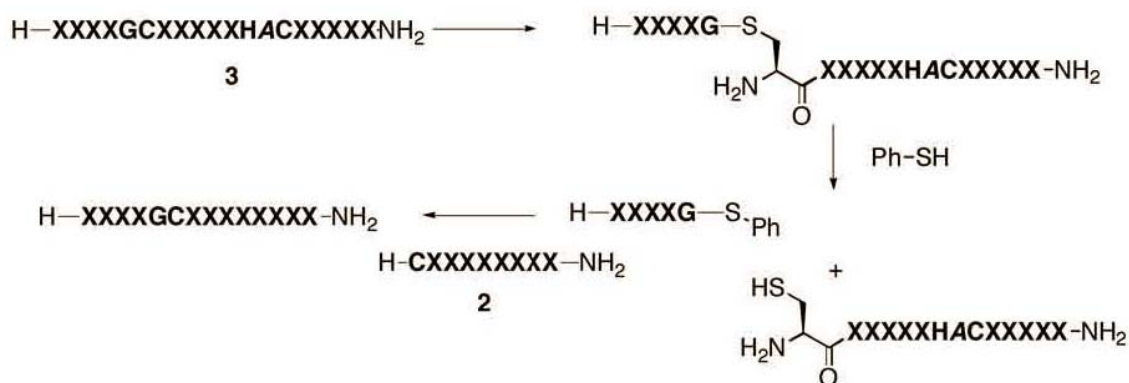
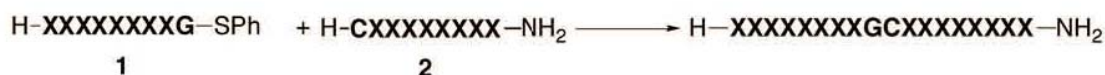
Explain the chemistry involved in **TWO** of the following methods for making amide bonds. [2×4]



Part C

Examine the following series of reactions of peptide sequences. All reactions take place in aqueous buffer.

- (i) Explain and give mechanisms for these transformations. [9]
- (ii) These reactions can take place in the absence of any *external* catalyst, but can nonetheless be subject to catalysis. Identify possible catalytic events and residues. [4]
- (iii) By considering the intermediates in your proposed mechanisms, suggest experiments that you could conduct to test your hypothetical mechanism. [4]



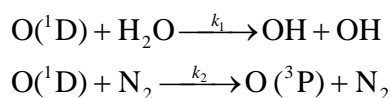
where **X = any amino acid**; all other amino acids are indicated in **bold** by their standard one letter abbreviation

QUESTION ENDS

11. Fundamentals of Atmospheric and Astrochemistry

Answer *three* of the following sections.

- A. (a) Ozone photolysis is an important process in the atmosphere, with an onset at $\lambda \approx 310$ nm. One of the products is $O(^1D)$; what is the other product, in what state is it principally formed and why?
- (b) During the daytime, a typical rate of absorption of radiation with $\lambda < 310$ nm by ozone in the lower atmosphere is 2.1×10^8 photons $s^{-1} cm^{-3}$ and the quantum yield for formation of $O(^1D)$ is 0.9. The $O(^1D)$ atoms are removed primarily by two processes



Calculate the rate of formation of OH radicals given that $k_1 = 2.2 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ and $k_2 = 1.8 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ at the appropriate temperature and that the mole fractions of H_2O and N_2 are 0.02 and 0.78 respectively. If the hydroxyl radical is removed in reactions for which the rate is given by the expression $60[OH] molecule cm^{-3} s^{-1}$, estimate the mean daytime concentration of OH under these conditions.

- B. (a) The mean temperature of the Earth's surface is higher than the mean temperature expected from the balance of absorbed and emitted radiation.
- (i) Explain qualitatively why this is so.
- (ii) Identify the atmospheric constituents which make major contributions to surface warming.
- (iii) Discuss how contributions of different gases depend on their concentrations.
- (b) According to a simple thermodynamic model, the temperature T of any planetary atmosphere should vary with altitude z according to

$$-\frac{dT}{dz} = \frac{g}{c_p}$$

where g is the acceleration of free fall and c_p is the constant pressure heat capacity per unit mass. (dT/dz from this equation is called the "dry adiabatic lapse rate".) Estimate c_p for the Earth's atmosphere below 80 km altitude, explaining the basis of your estimate and any necessary approximations. Hence calculate the dry adiabatic lapse rate using

the equation given.

[Take g to be 9.8 m s^{-2} .]

- C. (a) Briefly describe the operating principles behind cavity ringdown spectroscopy (CRDS).
- (b) The ringdown time, τ , for a cavity of length L formed by mirrors of reflectivity R and enclosing a homogeneous gas sample at concentration $[A]$ is

$$\tau = \frac{L}{c(1 - R + \sigma[A]L)}$$

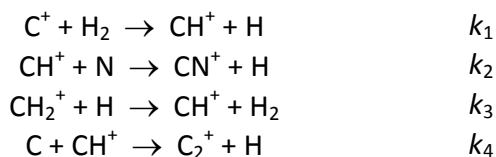
where c is the speed of light and σ is the (wavelength dependent) absorption cross-section of the sample.

The visible absorption spectrum of the NO_3 radical has a maximum absorption cross-section of value $2.2 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 662 nm. If a CRDS measurement conducted in 1 m long cavity displays a background ringdown time of $\tau_0 = 180 \mu\text{s}$ and a minimum detectable change, $\Delta\tau = 0.1 \mu\text{s}$, calculate:

- (i) the reflectivity, R , of the cavity mirrors;
- (ii) the detection limit for NO_3 in molecules cm^{-3} .
- (c) Discuss the role of NO_3 in the night time chemistry of the atmosphere.

- D. (a) Briefly discuss the events leading to star formation within a molecular cloud.

A simple model reaction scheme for some of the reactions involving the CH^+ ion within a molecular gas cloud is shown below.



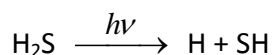
- (b) Use the steady-state approximation to derive an expression for the concentration of CH^+ . Assume that the number densities of all other species are known from astrochemical measurements.
- (c) Define the impact parameter for an ion-molecule collision.
- (d) At a given impact parameter, for which pair of reactants in the four elementary reactions above will the orbital angular momentum L be the highest? Calculate the

constant of proportionality between L and b for each of reactions 1 – 4 at a temperature of 50 K. You may make the (rather large) approximation that all collisions have a relative velocity equal to the mean relative velocity at this temperature, $v_{\text{rel}} = (8k_{\text{B}}T/\pi\mu)^{1/2}$.

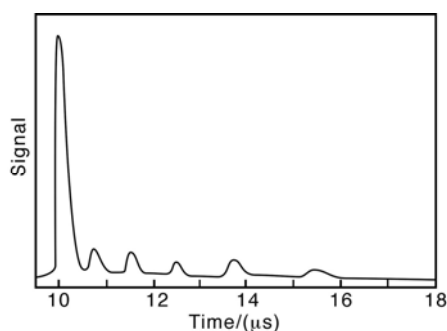
- (e) Which reaction is likely to be the rate determining step in the mechanism? Explain your answer.

12. Reaction dynamics

The photodissociation of H₂S at 193.3 nm



has been studied by timing the flight of the nascent H atoms to a detector 217 mm away. One such time-of-flight spectrum is shown below.



- (a) Show that the kinetic energy release (KER) in the photodissociation is given by the expression

$$\text{KER} = \frac{1}{2} m_{\text{H}} \left(1 + \frac{m_{\text{H}}}{m_{\text{SH}}} \right) \left(\frac{d}{t} \right)^2$$

where m_{H} and m_{SH} are the masses of the photofragments, t is the time of flight and d is the flight distance. Hence calculate the total kinetic energy release for a flight time of 10.0 μs . Given that the H-atom time-of-flight peak at 10 μs corresponds to formation of SH in its ground electronic and vibrational states, determine the dissociation energy of H₂S. [7]

Note: The relative atomic masses of H and S are 1 and 32 respectively.

- (b) Given that the second peak in the H-atom time-of-flight spectrum, which occurs at 10.74 μs , corresponds to the formation of H atoms in conjunction with SH formed in its first excited vibrational level, estimate the vibrational wavenumber of SH. [4]

Note: $1 \text{ cm}^{-1} = 11.96 \text{ J mol}^{-1}$

Question continues

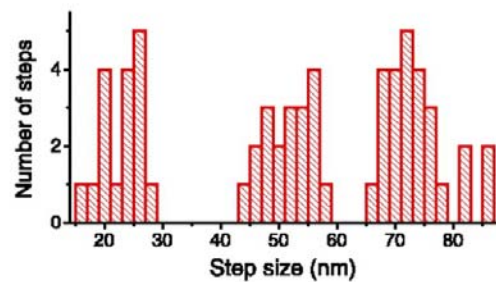
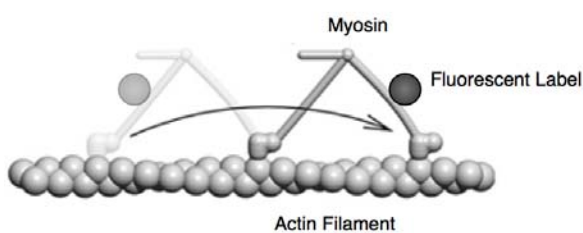
- (c) The H atoms produced from the photodissociation are found to be distributed preferentially perpendicular to the electric vector of the photolysis radiation. Comment on this observation. **[4]**
- (d) The nascent H atoms may then react with ozone: $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$. The OH product is found to be formed with a large amount of vibrational excitation with the maximum population in $v = 7$. What can you infer about the reaction dynamics given this observation? **[3]**
- (e) Draw a molecular orbital diagram for the SH product, and use it to predict the ground electronic state of this radical. You need only consider the $3p$ orbitals of sulphur, which lie higher in energy than the H atom $1s$ orbital. **[4]**
- (f) Discuss whether the H_2S photodissociation is spin-allowed. **[2]**
- (g) In the gas phase, the SH radical may be detected by observing the fluorescence induced by laser excitation (LIF) to the lowest excited state of $^2\Sigma^+$ symmetry. Use your molecular orbital diagram to identify the likely electronic configuration of this excited state. **[3]**
- (h) Both SH and SD may be detected using LIF but with different fluorescence quantum yields because of different predissociation rates in the excited electronic state. The rate constants for predissociation are $k_{\text{pre}}(\text{SH}) = 3.33 \times 10^8 \text{ s}^{-1}$ and $k_{\text{pre}}(\text{SD}) = 3.85 \times 10^6 \text{ s}^{-1}$ respectively.
- Note:** $\text{D} = ^2\text{H}$.
- (i) Discuss reasons for the difference in the two rate constants for predissociation. **[3]**
- (ii) Assuming that the A state can only undergo fluorescence and predissociation, and that the purely radiative lifetimes of SH and SD are both 775 ns, derive an equation for the quantum yield of fluorescence and determine its value for SH and for SD. **[4]**

13. Biophysical Chemistry

Answer ALL parts

Part A

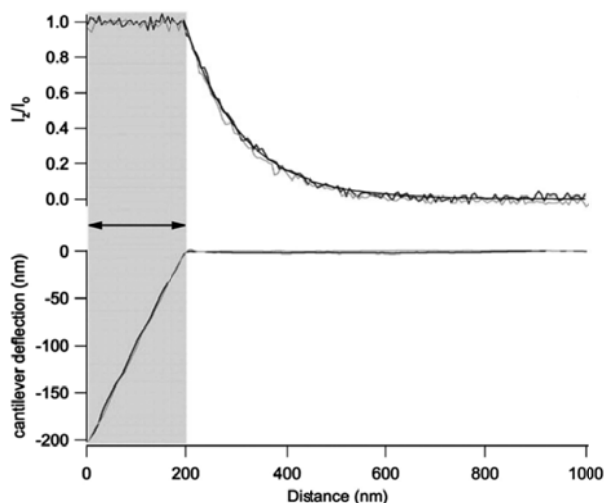
A fluorescent marker is placed at different locations on the light-chain domain of an individual myosin V molecule and individual steps along an actin filament recorded using single-molecule Total Internal Reflection Fluorescence Microscopy. The average step size is 37 nm.



- (a) Describe how in this experiment the position of the dye has apparently been determined to an accuracy smaller than the Abbé diffraction limit. [5]
- (b) If the dye is placed on the light-chain domain at a distance x along the direction of motion from the midpoint between the two heads of the motor, what step size do you expect to observe? [2]
- (c) What value of x explains the data shown in the figure? [3]
- (d) What do you suppose is the origin of the peak at approximately 74 nm in the step-size histogram? [1]

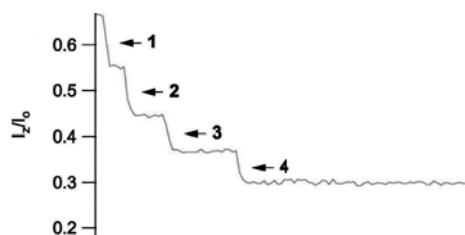
Part B

Simultaneous Total Internal Reflection Fluorescence Imaging and Atomic Force Spectroscopy are performed using a 200 nm fluorescent microsphere attached to the AFM cantilever. The following fluorescence intensity, and cantilever deflection traces were obtained.



- (e) Explain the shape of both Intensity and Deflection traces. What does the shaded region marked by the arrow correspond to? [3]
- (f) Calculate the penetration depth associated with the exponential decay. [3]

The combined AFM/TIRF microscope was used to extend a polyubiquitin protein in a constant-force pull-off experiment. The normalised fluorescence response (I_z/I_0) from the fluorescent microsphere attached to the cantilever is show below.



- (g) What is happening at each of the four events indicated on the diagram? [1]
- (h) Why does each change in intensity appear to take longer as time progresses? [1]
- (i) Comment on the change in the magnitude of I_z/I_0 with each step. [1]

- (j) Intensities before and after an individual step transition are 800 counts and 670 counts respectively. Using your estimate of penetration depth from part (g), calculate the contour length of ubiquitin. [2]

Part C

The molecular weight of a 5-residue peptide, X, was determined as 607.22 Da using MALDI mass spectrometry. To determine its sequence the peptide was treated with the reducing agent DTT and iodoacetic acid, and a tandem mass spectrum (MS/MS) was recorded (below)

- (k) Draw the major product ions that may be produced upon collision-induced dissociation of this peptide inside the mass spectrometer [2]
- (l) Explain the origin of each of the peaks obtained in the MS/MS spectrum, using this information assign the sidechains (R1-5) in the peptide to determine the sequence of the peptide. Atomic and amino acid residue masses are given in the attached table. [7]
- (m) How does the mass of this peptide compare to that measured for the intact unmodified peptide? Comment on any structural implications. [2]

Amino Acid	3 Letter Code	Single Letter Code	Amino Acid mass (Da) (monoisotopic)	Residue Mass (Da) (monoisotopic)
Glycine	Gly	G	75.03	57.02
Alanine	Ala	A	89.05	71.04
Serine	Ser	S	105.04	87.03
Proline	Pro	P	115.06	97.05
Valine	Val	V	117.08	99.07
Threonine	Thr	T	119.06	101.05
Cysteine	Cys	C	121.02	103.01
Isoleucine	Ile	I	131.09	113.08
Leucine	Leu	L	131.09	113.08
Asparagine	Asn	N	132.05	114.04
Aspartic Acid	Asp	D	133.04	115.03
Glutamine	Gln	Q	146.07	128.06
Lysine	Lys	K	146.10	128.09
Glutamic Acid	Glu	E	147.05	129.04
Methionine	Met	M	149.05	131.04
Histidine	His	H	155.07	137.06
Phenylalanine	Phe	F	165.08	147.07
Arginine	Arg	R	174.11	156.10
Tyrosine	Tyr	Y	181.07	163.06
Tryptophan	Trp	W	204.09	186.08
Modified Amino Acids				
Carboxymethylcysteine			179.02	161.01
Atoms				
H			1.01	-
O			15.99	-
C			12.01	-

14. Theoretical chemistry

Answer ALL parts

Part A.

- (a) The Einstein B coefficient for the induced absorption and emission of electromagnetic radiation *in vacuo* is

$$B = \frac{\pi |\mu_{ij}|^2}{3\varepsilon_0 \hbar^2}$$

where μ_{ij} is the transition dipole moment between states $|i\rangle$ and $|f\rangle$.

Using the principle of detailed balance, derive the Einstein A coefficient for the spontaneous emission of electromagnetic radiation. [8]

You may use the information that the energy density of black body radiation per unit angular frequency, ω , is

$$U(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 (\exp(\hbar\omega/k_B T) - 1)}$$

- (b) Calculate the spontaneous and induced emission rate from the 2p level of the hydrogen atom at 1,000K.

[9]

Note that,

$$\psi_{n=1,\ell=0,m=0} = \frac{1}{\sqrt{\pi a_\mu^3}} \exp(-r/a_\mu)$$

$$\psi_{n=2,\ell=1,m=0} = \frac{1}{\sqrt{32\pi a_\mu^5}} \exp(-r/2a_\mu) r \cos\theta$$

$$a_\mu = 5.29 \times 10^{-11} m, \text{ and } R_H = 2.18 \times 10^{-18} J.$$

Part B.

- (a) The equation of state for the van der Waals gas is given by

$$p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

and exhibits a critical point at $V_c = 3Nb$ and $kT_c = 8a/27b$.

Calculate $(\partial p / \partial V)_T$ at $V = V_c$, and hence show that the isothermal compressibility κ_T , which is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial p}{\partial V} \right)^{-1},$$

scales as $\kappa_T \sim (T - T_c)^{-\gamma}$ [6]

- (b) The Hamiltonian for the Ising model is given by

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - B \sum_i S_i$$

where $\langle i, j \rangle$ signifies the sum is over nearest neighbours, B is the magnetic field and the spins S_i can take the values ± 1 .

Outline how the mean-field partition function for the Ising model is obtained. Namely,

$$Z_{MF} = \exp\left(-\frac{\beta J m^2 N z}{2}\right) \left[2 \cosh\left(\frac{m J z + B}{k_B T}\right)\right]^N$$

where z is the coordination number of the lattice and m is the magnetization per spin. [5]

Given that $(\partial A / \partial B)_T = -M$, where A is the Helmholtz free energy and M the magnetization, show that m obeys [3]

$$m = \tanh[\beta(Jzm + B)].$$

Hence, obtain the mean-field expression for the critical temperature. [3]

Advanced Structural, Scattering and Surface Methods - Sample paper question

1. The formula below represents one of the important scattering laws:

$$I(k) = I_0 \exp\left(-\frac{1}{3}R_g^2 k^2\right).$$

(a) Describe the quantities I , k , I_0 , and R_g in this equation. [3]

(b) Is this the Guinier or the Porod law? When can the above equation be used and what information can be obtained from it. [6]

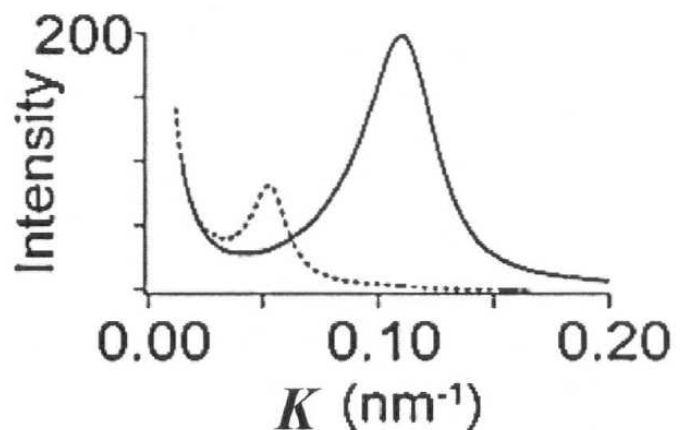
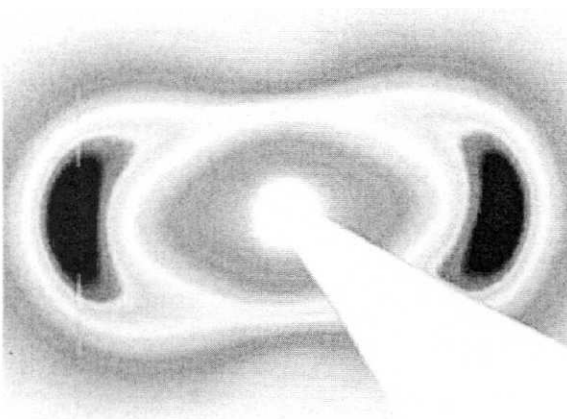
(c) Expand the equation above up to k^2 for small k and replace R_g^2 by $\frac{3}{5}a^2$ with a the radius of a sphere. [4]

(d) The form factor $P(k)$ for a spherical particle can be written as

$$P(k) = \left[3 \frac{\sin(x) - x \cos(x)}{x^3}\right]^2,$$

with $x = ka$. Expand the numerator of the above equation up to x^5 for small x (i.e. the first 3 non-zero terms for the sin and the first 2 non-zero terms for the cos), and show that it leads to the same expression as under (c). [6]

The x-ray scattering pattern below corresponds to a liquid crystalline phase of board-like colloidal particles. The graph on the right shows the intensity profiles in the horizontal (solid line) and the vertical (dashed line) directions. Clear peaks are observed at $k_1 = 0.11 \text{ nm}^{-1}$ and $k_2 = 0.05 \text{ nm}^{-1}$, respectively. The x-ray wavelength was $\lambda = 0.1 \text{ nm}$.



(e) Sketch a possible arrangement of the board-like colloidal particles [3]

- (f) What is the characteristic distance between the particles in the horizontal and vertical directions? [4]
- (g) Calculate the scattering angle θ corresponding to these values of k_1 and k_2 . [4]
- (h) Imagine that one studies the same board-like colloidal particles as in part (d) and (e), but now using a HeNe laser with a wavelength $\lambda = 628$ nm. What is the maximum k value that can be reached in this light scattering experiment? [4]

16. Magnetic resonance

Answer all parts

- (a) The time-dependent wavefunction $|\Psi\rangle(t)$ of a system may be written as a linear combination of the eigenstates $|n\rangle$ of the Hamiltonian \hat{H} of the system

$$|\Psi\rangle(t) = \sum_n c_n(t) |n\rangle$$

where the time-dependence of the coefficients $c_n(t)$ is given by

$$c_n(t) = c_n(0) \exp(-iE_n t / \hbar)$$

and E_n is the energy of state $|n\rangle$. Show that $|\Psi\rangle(t)$ satisfies the time-dependent Schrödinger equation. [4]

- (b) The eigenstates of an isolated spin- $\frac{1}{2}$ nucleus in a strong magnetic field are $|\alpha\rangle$ and $|\beta\rangle$. In this $\{\alpha, \beta\}$ basis, the matrix representation of an operator \hat{A} is defined as

$$\mathbf{A} = \begin{pmatrix} \langle \alpha | \hat{A} | \alpha \rangle & \langle \alpha | \hat{A} | \beta \rangle \\ \langle \beta | \hat{A} | \alpha \rangle & \langle \beta | \hat{A} | \beta \rangle \end{pmatrix}$$

The matrix representations of the angular momentum operators \hat{I}_x and \hat{I}_y in the $\{\alpha, \beta\}$ basis are

$$\mathbf{I}_x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \hbar; \quad \mathbf{I}_y = \begin{pmatrix} 0 & -\frac{1}{2}i \\ \frac{1}{2}i & 0 \end{pmatrix} \hbar$$

Use the relation $[\hat{I}_x, \hat{I}_y] = i\hbar\hat{I}_z$ to verify that the matrix representation of \hat{I}_z is

$$\mathbf{I}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \hbar$$

What are the eigenvalues and eigenstates of \hat{I}_z ? [2]

- (c) Show that the expectation value of an operator \hat{A} is given by

$$\langle \hat{A} \rangle = \text{trace}[\mathbf{A} \cdot \boldsymbol{\rho}(t)]$$

where $\boldsymbol{\rho}(t)$ is a matrix whose elements $\rho_{nm}(t)$ are equal to $c_n(t)c_m^*(t)$.

Note: the trace of a matrix is the sum of its diagonal elements. [4]

- (d) Use your results from (b) and (c) to derive expressions for the expectation values $\langle \hat{I}_x \rangle$, $\langle \hat{I}_y \rangle$ and $\langle \hat{I}_z \rangle$ in terms of the coefficients $c_\alpha(t)$ and $c_\beta(t)$. [6]

- (e) The spin Hamiltonian of the nucleus in part (b) may be written

$$\hat{H} = -\omega \hat{I}_z$$

where $\omega = (1 - \sigma)\omega_0$.

- (i) Comment on the significance of the quantity $(1 - \sigma)\omega_0$. [3]
- (ii) Consider a system prepared in the initial state $c_\alpha(0) = 1$; $c_\beta(0) = 0$. Derive expressions for the time-dependence of $\langle \hat{I}_x \rangle$, $\langle \hat{I}_y \rangle$ and $\langle \hat{I}_z \rangle$ in terms of \hbar and ω . [4]
- (iii) Repeat this calculation for the initial state $c_\alpha(0) = c_\beta(0) = 1/\sqrt{2}$. [4]
- (iv) Comment on the differences between your results in (ii) and (iii) in terms of the vector model of magnetic resonance. Discuss how the initial state in (iii) could be created from that in (ii). Include in your answer an explanation of how your results relate to the spectrum obtainable in a simple NMR experiment. [7]