

SECOND PUBLIC EXAMINATION

Honour School of Natural Science

CHEMISTRY PART IB

INORGANIC CHEMISTRY

OPTION 2

FRONTIERS OF INORGANIC CHEMISTRY

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.

DO NOT TURN OVER until told that you may do so

Biological and Coordination Chemistry

1. Answer *either* part **A** *or* part **B**.

A. Give an account of (i) anion coordination chemistry; (ii) ligand preorganisation; and (iii) self-assembly in inorganic chemistry. [50]

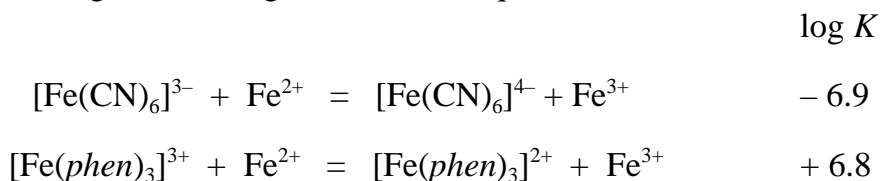
B. Discuss the factors which affect the magnitude of stability constants in aqueous solution with particular reference to some or all of the data shown below.

[50]

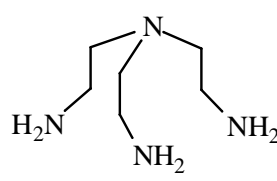
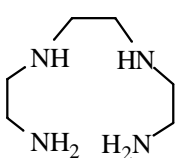
(a) For the dicarboxylates:

| | log K_1 | |
|------------------|--|---|
| | $^{-}\text{O}_2\text{C}-\text{CO}_2^{-}$ | $^{-}\text{O}_2\text{CCH}_2\text{CO}_2^{-}$ |
| Be^{2+} | 4.96 | 6.18 |
| Mg^{2+} | 3.43 | 2.85 |
| Pb^{2+} | 4.91 | 3.68 |

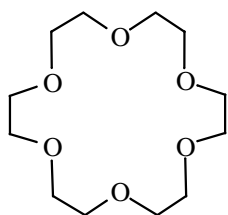
(b) The ligand exchange reactions in aqueous solution:



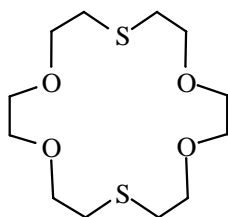
(c) For the amines:

| | | | | |
|---|---|------------------|------|------------------|
|  <p style="text-align: center;"><i>Tren</i></p> | log K | | | |
| | <table> <tbody> <tr> <td>Zn^{2+}</td> <td>14.7</td> </tr> <tr> <td>Cu^{2+}</td> <td>19.0</td> </tr> </tbody> </table> | Zn^{2+} | 14.7 | Cu^{2+} |
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|  <p style="text-align: center;"><i>Trien</i></p> | log K | | | |
| | <table> <tbody> <tr> <td>Zn^{2+}</td> <td>12.1</td> </tr> <tr> <td>Cu^{2+}</td> <td>20.4</td> </tr> </tbody> </table> | Zn^{2+} | 12.1 | Cu^{2+} |
| Zn^{2+} | 12.1 | | | |
| Cu^{2+} | 20.4 | | | |

(d) For the crown ligands:

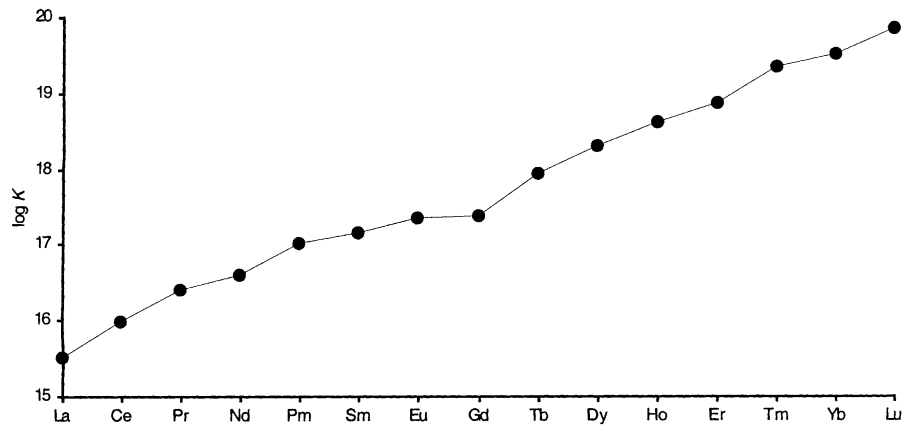


| | $\log K$ |
|--------|-------------|
| K^+ | 6.10 (MeOH) |
| Ag^+ | 1.60 |



| | $\log K$ |
|--------|-------------|
| K^+ | 1.15 (MeOH) |
| Ag^+ | 4.34 |

(e) For the formation of 1:1 complexes of lanthanide Ln^{3+} ions with $EDTA^{4-}$:



2. Answer *either* part **A** *or* part **B**.

A. Discuss the chemical principles underlying *three* of the following:

[3 × 50/3]

- (a) Iron transport by siderophores and transferrin.
- (b) The chemistry of cobalt complexes and its relationship to that of coenzyme B₁₂.
- (c) The chemistry of M_nS₄ clusters (where M is a metallic element and n = 3 or 4) and their role in proteins and enzymes.
- (d) Oxo-molybdenum centres and iron-containing monooxygenases in the transfer/insertion of oxygen atoms into substrates.
- (e) Nitrogen fixation.

B. Give an account of *one* of the following:

[50]

- (a) The role of metals in medicine. Your account should include both the *cisplatin* family of anticancer drugs and more recent approaches in designing metal complexes that are selectively sequestered into hypoxic cancer cells.
- (b) Electron transfer in biology. Discuss the factors controlling electron transfer kinetics on the basis of Marcus theory, in particular the effect of donor-acceptor separation and reorganisation energy. You may wish to include some of the following systems: photosystem II, the cytochrome *c*/cytochrome *c* oxidase reaction, plastocyanins, iron-sulphur proteins.
- (c) About 30% of the human genome now appears to encode ‘zinc finger’ domains. Explain what a zinc finger domain is and outline how such a zinc-binding site is identified at the gene level. Zn is also used in enzymes with hydrolytic (carboxypeptidase) and redox (alcohol dehydrogenase) activities. Speculate on why biology has chosen Zn for these purposes and how Zn proteins can be studied with spectroscopic methods.

Organometallic Chemistry

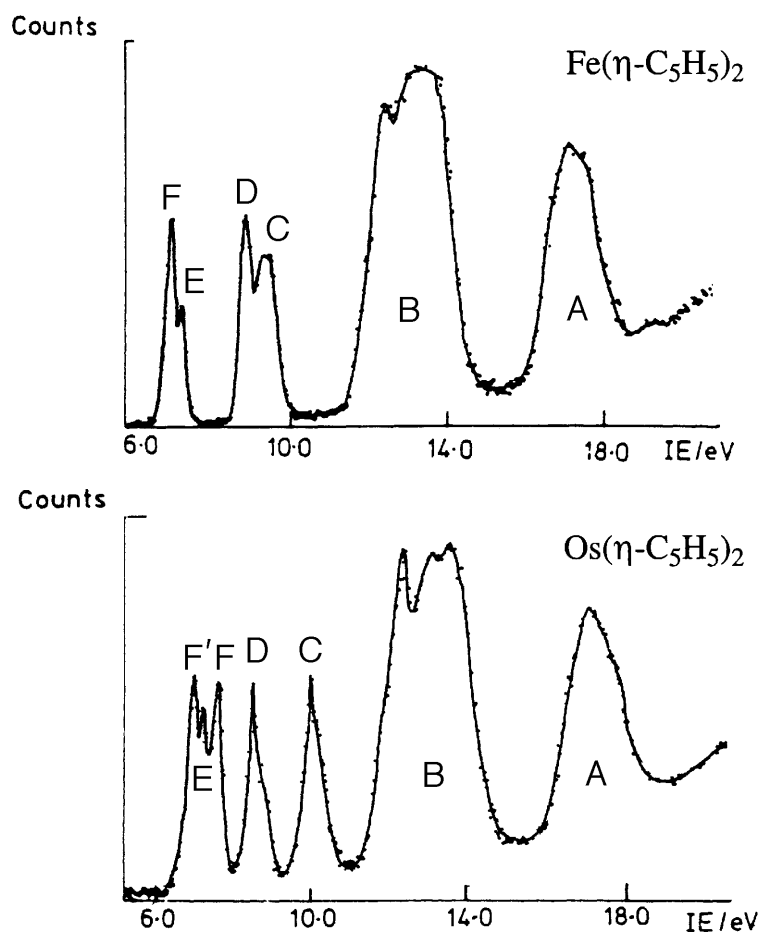
3. Answer *either* part A or part B.

A. Write an essay on the structure and bonding in (i) metal-carbene, and (ii) metal-olefin complexes. Include in your account a discussion of how the variation in bonding characteristics affects the reactivity of the respective groups. [50]

B. Answer *all* of the parts (a) – (c).

(a) Construct a molecular orbital energy level diagram for metallocene compounds $M(\eta\text{-C}_5\text{H}_5)_2$ with a staggered geometry. [20]

(b) Hence or otherwise suggest assignments for the photoelectron spectra of $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Os}(\eta\text{-C}_5\text{H}_5)_2$ shown below. Note that band **F** in the spectrum of $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ is split into two bands, **F** and **F'**, of equal intensity in the spectrum of $\text{Os}(\eta\text{-C}_5\text{H}_5)_2$. Assignments of the broad bands **A** and **B** are *not* required. [15]



- (c) Comment on the M–C distances ($r_{\text{M-C}}/\text{\AA}$) and effective magnetic moments ($m_{\text{eff}}/\mu_{\text{B}}$) at room temperature of the metallocene compounds $\text{M}(\eta\text{-C}_5\text{H}_5)_2$: [15]

| M = | V | Cr | Mn | Fe | Co | Ni |
|---------------------------------|------|------|------|------|------|------|
| $r_{\text{M-C}}/\text{\AA}$ | 2.56 | 2.32 | 2.72 | 2.10 | 2.20 | 2.33 |
| $m_{\text{eff}}/\mu_{\text{B}}$ | 3.84 | 3.20 | 5.81 | 0 | 1.76 | 2.86 |

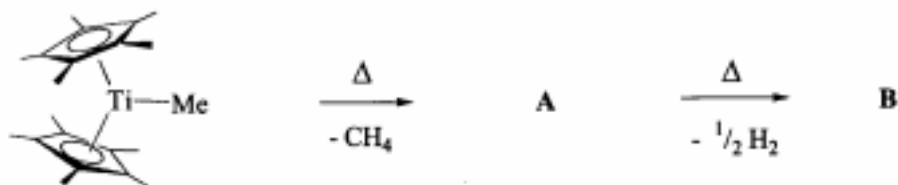
4. Answer *either* part **A** *or* part **B**.

A. Write a concise account of *two* of the following topics, (a) – (d). (2 × 25)

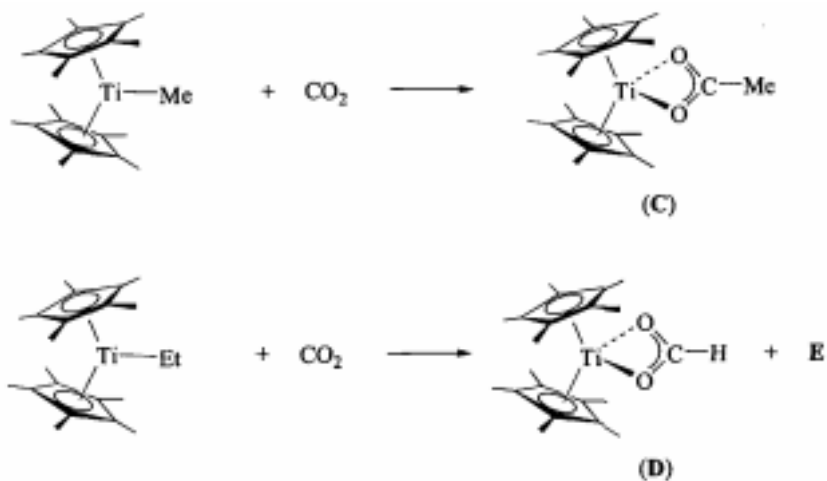
- (a) The polymerization of alkenes using transition metal catalysts. Include in your answer a range of examples from both the early and later transition metals with both cyclopentadienyl and non-cyclopentadienyl supporting ligands.
- (c) The synthesis and reactions of transition metal compounds with metal-carbon multiple bonds.
- (d) The homogeneous catalytic hydrogenation and hydroformylation of alkenes using transition metal compounds. Where relevant, indicate how regio- and stereo-selectivity has been achieved.

B. Answer *all* of the parts (a) - (d) which relate to some aspects of the organometallic chemistry of titanium.

- (a) Identify the compounds **A** and **B** in the following reaction sequence and comment on the reaction mechanism for the formation of compound **A**.



- (b) For the following balanced reactions, describe the mechanisms leading to compounds **C** and **D**, and identify the organic product **E**.



- (c) Treatment of a toluene solution of $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$ with an excess of methyl aluminoxane (MAO) in toluene under a 5 bar pressure atmosphere of ethane leads to a rapid temperature rise and eventually to the formation of a thick white precipitate.

Comment on the reactions taking place in solution, and the nature of any likely organometallic intermediates and reaction products. What would be the outcome of this reaction if it were carried out in the presence of propene instead of ethene?

- (d) Treatment of TiCl_4 at low temperature with four equivalents of MeMgI gives a homoleptic, organometallic compound **F** that is thermally unstable above $40\text{ }^\circ\text{C}$. However, treatment of **F** with the chelating ligand 2,2'-bipyridine affords a derivative **G** which is moderately stable at ambient temperatures. The corresponding reaction of TiCl_4 with EtMgBr gives a product **H** that is unstable above $-70\text{ }^\circ\text{C}$. In contrast, reaction of TiCl_4 with four equivalents of $\text{LiCH}_2\text{SiMe}_3$, gives the compound **I** which is reasonably stable at room temperature in the absence of light, oxygen and water.

Reaction of TiCl_4 with four equivalents of PhCH_2MgBr gives an organometallic compound **J** which is also reasonably stable at room temperature in the absence of light, oxygen and water. Compound **J** has relatively acute Ti-CH-Ph angles in the solid state.

Reaction of TiCl_4 with four equivalents of NaC_5H_5 afforded the fluxional compound **K** which is thermally stable in solution at temperatures up to at least $80\text{ }^\circ\text{C}$. The ^1H NMR spectrum of **K** in solution shows temperature-dependent behaviour. At $80\text{ }^\circ\text{C}$ a single sharp resonance is observed. On cooling to *ca.* $-40\text{ }^\circ\text{C}$ this signal broadens, and then decoalesces to form two singlets of equal intensity. On further cooling one of these broadens further and eventually gives rise to three further multiplets of relative intensity 2:2:1.

All of the compounds **F** – **K** are diamagnetic. They all contain only the elements C, H and Ti, with the exception of **G** which also contains N, and **I** which also contains Si; none contain Cl. Identify the compounds **F** to **K** and account for their ground state molecular structures and relative thermal stabilities. Identify the fluxional processes occurring for compound **K**.

Solid State Chemistry

5. Answer *one* of the Parts A – C [50]

- A. Give an account of the inherent problems encountered in the solid state synthesis of a compound. What strategies can be adopted to overcome these difficulties?

Outline how you would effect four of the following syntheses (i) – (vi).

- (i) Prepare diamond from graphite
- (ii) Prepare a superconducting sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.
- (iii) Grow a single crystal of Mg_2SiO_4 .
- (iv) Prepare a crystalline sample of Na_xWO_3 .
- (v) Prepare a sample of LiMnO_2 with ordered cations.
- (vi) Prepare a sample of the mesoporous zeolite MCM-41.

- B. “There are two descriptions of the electron in a solid, the localised picture and the itinerant electron model.” Discuss the validity of this statement with reference to some of the following materials and, if you wish, to additional examples of your own choosing:

| | | | |
|---|--|---------------------------|----|
| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | Fe_3O_4 | VO_2 | Fe |
| $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ | CrO_2 | Bi_2RuO_7 | |
| Y_2RuO_7 | $\text{K}_2\text{Pt}(\text{CN})_4 \cdot \text{Br}_{0.3}$ | Na | |

What experimental techniques would you use to establish which model gives the better account of a newly prepared compound? [33]

- C. Write an essay on the preparation, structure and chemical properties of intercalation compounds with lamella hosts. Provide examples of techniques by which the guest species can be studied. Examples of hosts you may wish to include are: graphite, layered metal chalcogenides such as TaS_2 , layered metal oxychlorides such as FeOCl , V_2O_5 , MoO_3 , $\text{Zr}(\text{HPO}_4)_2$, $\text{Zr}(\text{RPO}_3)_2$, LiCoO_2 , layered silicate minerals and clays.

6. Answer part **A** *and* part **B**.

A. Write short notes on *either* superconductivity *or* fast ion conductors. (50/3)

B. Account for *two* of the following observations (a) – (c). (2 × 50/3)

(a) LaMnO_3 is an antiferromagnetic insulator with a Neel temperature of 140 K. It has a perovskite-type structure, in which each Mn is coordinated by $4 \times \text{O}$ at 201 pm and $2 \times \text{O}$ at 216 pm.

In contrast CaFeO_3 is a metallic conductor at room temperature. It also has a perovskite structure, but Fe is coordinated by $6 \times \text{O}$ at 193 pm. On cooling below 115 K, CaFeO_3 becomes a semiconductor. The low temperature structure has Fe in two types of regular octahedral environment; Fe-O distances of 189 pm for one site and 197 pm for the other.

(b) At 300 K both the X-ray and neutron diffraction patterns of MnO are indexed on a face-centred-cubic unit cell, with a cell constant $a = 460$ pm. At 80 K the X-ray pattern appears similarly face-centred-cubic, with a cell constant of $a = 442$ pm. The neutron diffraction pattern, however, shows extra reflections and is indexed as face-centred-cubic with a cell constant of $a = 884$ pm. A high resolution X-ray diffraction pattern shows that the low temperature structure of MnO only approximates to cubic and is in fact trigonally distorted into a rhombohedral ($a = b = c$, $\alpha = \beta = \gamma = 89.4^\circ$) structure.

(c) The bandgaps of GaAs, InAs and InSb are respectively 1.35 eV, 0.35 eV and 0.163 eV. Substituting Al for Ga in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ increases the bandgap. In the solid solutions $\text{InSb}_{1-x}\text{As}_x$ the bandgap passes through a minimum of 0.13 eV at $\text{InSb}_{0.9}\text{As}_{0.1}$. In mercury cadmium telluride (MCT), $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, the bandgap can be tuned from 0 eV through to 1.44 eV. MCT materials are useful infrared detectors.