

Inorganic Chemistry

Part IA

Sample Paper

Candidates should answer *SIX* questions in 2½ hours

Numbers in square brackets indicate the approximate weight to be given to each part of the question

1. Answer **three** of the following parts. [3 × 20/3]

(i) Determine the point group of **one** of the following compounds and indicate the symmetry elements involved on a sketch of the structure:



(ii) Which of the following complexes obey the eighteen electron rule?



(iii) What isomers are possible for complexes of the following empirical formulae?



(iv) Derive the term symbol for the ground state in the gas phase of **three** of the following ions:



(v) Determine the number of ir active element-halogen stretching vibrations for **one** of the following:



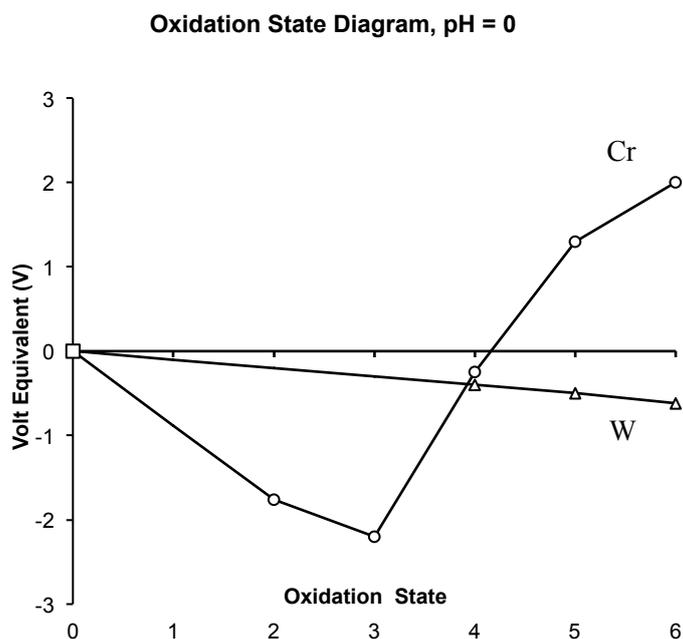
2. Answer **all** parts.

- (i) Discuss the following values for the ligand field splitting parameter Δ in some octahedral complexes: [6]

	Δ / cm^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22900
$[\text{Co}(\text{NH}_3)_6]^{2+}$	10200
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34100
$[\text{Co}(\text{OH}_2)_6]^{3+}$	20700
$[\text{Fe}(\text{CN})_6]^{3-}$	35000
$[\text{Fe}(\text{CN})_6]^{4-}$	34000

- (ii) Discuss the observation that $[\text{NiCl}_4]^{2-}$ and PdF_2 are paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$ are diamagnetic. [6]

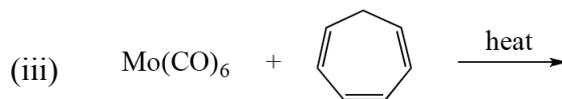
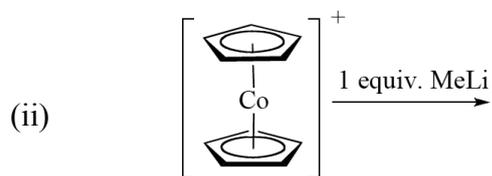
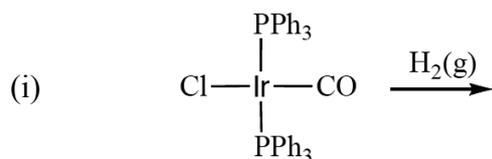
- (iv) Discuss the occurrence, the nature of the species and the stability trends in the oxidation state diagram below for Cr and W at 25 °C and pH 0: [8]



3. Answer **both** Part A and Part B.

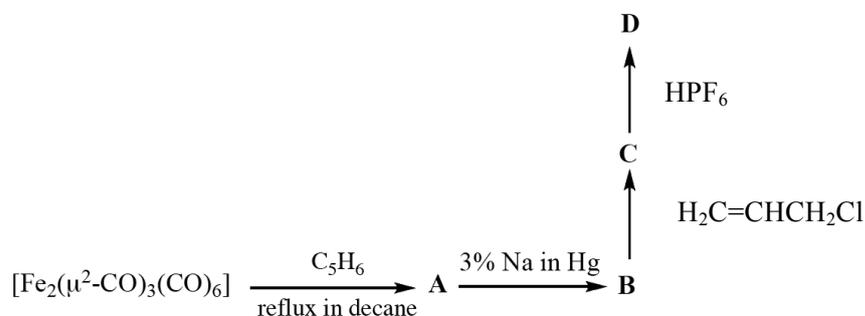
(A) Identify the organometallic product for **three** of the following reactions (i)–(iv). Draw the structure of the transition metal product. Give the valence electron count of **both** the organometallic reactants and products.

[4 × 3]



Question continues

- (B) Identify the organometallic products **A** to **D** in the following reaction sequence and give their structures. Make full use of the data given and show your reasoning clearly. Indicate the structures of the products you suggest. [8]



Compound **A** is a binuclear compound with elemental composition Fe% 31.56, C% 47.51, O% 18.10, H% 2.82. It has two very different $\nu(\text{CO})$ bands in its infrared spectrum at 1960 cm^{-1} and 1765 cm^{-1} .

Compound **B** is a water-sensitive salt which has two $\nu(\text{CO})$ bands in its infrared spectrum at 2015 cm^{-1} and 1910 cm^{-1} .

Compound **C** has a mass spectrum showing a molecular ion at $m/z = 217.8$ and further peaks at $m/z = 189.8$ and 161.8 .

Compound **D** is a water-sensitive salt containing an 18-electron cation which has two $\nu(\text{CO})$ bands in its infrared spectrum.

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

4A. Answer **all** the parts (a)–(e):

- (a) Describe the pattern of systematic absences in x-ray powder diffraction patterns of face centred cubic and body centred cubic materials. [2]
- (b) Reaction between Au powder and molten Cs yields a compound *A* whose X-ray powder diffraction pattern gives lines with the following *d* spacings.

<i>d</i> spacing / pm	Intensity
426.3	very weak
301.4	very strong
246.1	very weak
213.2	strong
190.6	very weak
174.0	strong
150.7	medium

Index the pattern and derive a value for the cubic lattice parameter. [5]

- (c) The compound *A* contains 59.7% Au by mass and has a density of 7.072 g cm⁻³. Deduce the empirical formula of *A* and the number of formula units per cell. Hence suggest a structure for *A* and derive a value for the shortest Cs–Au distance. [4]
- (d) Explain qualitatively why some lines in the powder diffraction pattern of *A* are very weak. How would the X-ray powder diffraction pattern of CsI differ qualitatively from that of *A*? [5]
- (e) Given the following additional information:

Metallic radii: Cs: 266 pm; Au: 144 pm.

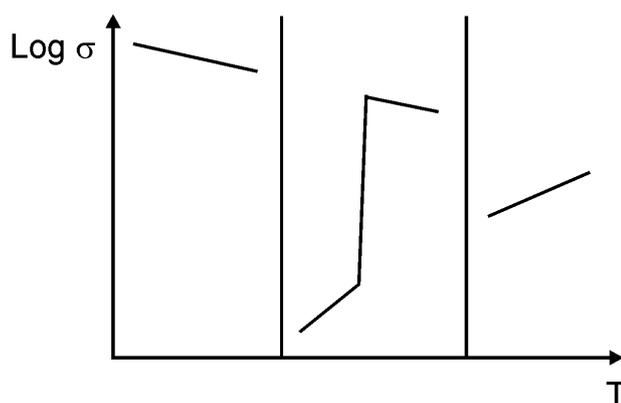
Electronegativities: Cs: 0.79; Au: 2.54; I: 2.66.

Suggest what the physical appearance of the compound would be and how well you would expect it to conduct electricity. [4]

(RAMs: Cs 132.9; Au 197.0. Avogadro number = $6.022 \cdot 10^{23} \text{ mol}^{-1}$)

4B. Answer **two** of Parts (a)–(c).

- (a) (i) Sketch a molecular orbital diagram showing the valence orbitals for the species $[\text{PtH}_4]^{2-}$. [2]
(ii) Use these molecular orbitals as the basis for a qualitative sketch of the electronic band structure of a one-dimensional stack of planar $[\text{PtH}_2]^{2-}$ ions. Locate the Fermi level clearly on your diagram. [5]
(iii) How would the diagram be modified for a stack of $[\text{IrH}_4]^{2-}$ ions? Comment on the difference in physical properties you might expect for these two hypothetical systems. [3]
- (b) (i) The variation of the electronic conductivities with temperature of ReO_3 , VO_2 and pure Si are shown qualitatively in the diagram, but not necessarily in that order. Identify which solid has which dependence and explain the temperature dependence of the conductivity in each case. [6]

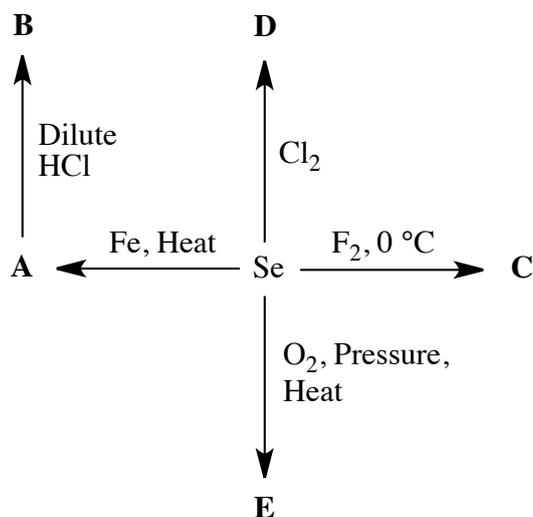


- (ii) Sketch the temperature dependence you would expect for silicon which has been very lightly doped with phosphorus. [4]
- (c) The following transition metal dioxides all adopt rutile-related structures. Explain why they show a great range of electronic properties at ambient temperatures. [10]

TiO_2	Insulator
VO_2	Metal above 340 K; insulator below 340 K
MnO_2	Insulator
NbO_2	Insulator
RuO_2	Metal
SnO_2	Insulator

[Note that NbO_2 and the low temperature form of VO_2 have distorted variants of the rutile structure.]

5. Answer **all** parts.



- (a) Heating Se with metallic iron readily forms the solid **A** containing 41.40% Fe and 58.60% Se. Treatment of **A** with dilute aqueous HCl gives off a toxic gas **B** containing 97.53% Se.
- Identify and suggest structures for **A** and **B**. [4]
 - Explain why **B** is less stable to decomposition than the analogous sulfur compound. [2]
 - Comment on the observation that the pK_a of **B** is 3.9 while that of the sulfur analogue is 6.9. [3]
- (b) The reaction between Se and F_2 at 0°C gives **C** (RMM = 155) which has a dipole moment. Identify **C** and predict its ^{77}Se NMR spectrum at -50°C . [4]
- (c) Treatment of Se with Cl_2 gives a solid **D** containing 35.75% Se. Identify **D** and comment on the observation that the analogous compound of sulfur is unknown. [3]
- (d) Heating Se under O_2 pressure gives a white solid **E** containing 71.17% Se. **E** readily dissolves in water to give an oxy-acid with $pK_1 = 2.5$.
- Identify **E** and account for the pK_1 value of the oxy-acid. [2]
 - Comment on the observation that the analogous reaction between sulfur and oxygen, although extremely slow, gives a product with a different stoichiometry. [2]

[Relative atomic masses: Se 79.0, Fe 55.8, Cl 35.5, F 19.0, O 16.0, H 1]

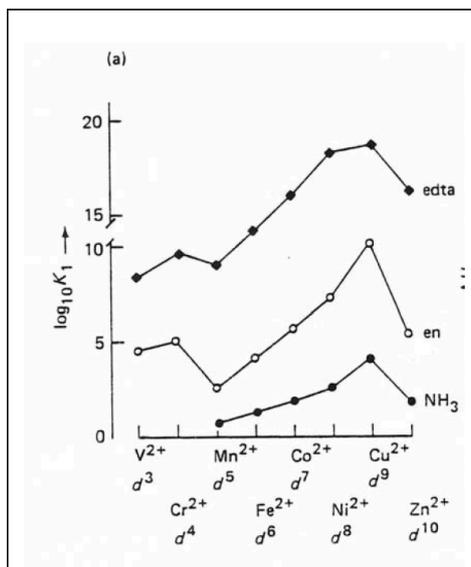
6. Answer **all** of the following parts, providing explanations where possible:

(i) What are the chelate and macrocyclic effects? [4]

(ii) Give an expression in terms of concentrations for the STEPWISE stability constants K_1 and K_2 for the reaction of $[M(H_2O)_6]^{2+}$ with ligand L. [2]

(iii) Why are octahedral Cu^{2+} complexes often distorted from regular octahedral geometry? What is the driving force for this distortion and how does it affect the value of K_1 ? [4]

(iv) Account for the trends in stability constants shown in the figure below. [10]



7. Answer **all** of the parts (a)–(d).

(a) Construct an MO energy level diagram for the σ -bonding framework of SiF_4 , assuming it adopts a tetrahedral (T_d) geometry. Sketch the form of the full and empty MOs in terms of a linear combination of atomic orbitals (for degenerate levels you only need show the form of the MO for one component). [6]

(b) How would your MO diagram be modified if Si were replaced with S while maintaining the same tetrahedral geometry? Derive values for the formal bond orders in tetrahedral SiF_4 and SF_4 . [3]

(c) Making use of the descent in symmetry table provided below, suggest *two* alternative geometries for SF_4 that would energetically stabilise the molecule.

Draw sketches of the two different structures and discuss them in relation to the valence shell electron pair repulsion (VSEPR) model. [5]

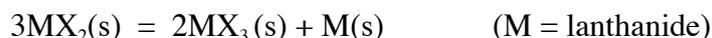
(d) The room-temperature ^{19}F NMR spectrum of SF_4 reveals a single ^{19}F resonance which upon cooling gives rise to two 1:2:1 triplet resonances of equal intensity. The IR spectrum reveals four IR-active S-F stretching modes. Explain fully which geometry of SF_4 is consistent with these data. [6]

T_d	T	D_{2d}	C_{3v}	C_{2v}
A_1	A	A_1	A_1	A_1
A_2	A	B_1	A_2	A_2
E	E	$A_1 + B_1$	E	$A_1 + A_2$
T_1	T	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$
T_2	T	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$

[^{19}F , $I = \frac{1}{2}$, 100%. The influence of other nuclei can be ignored.]

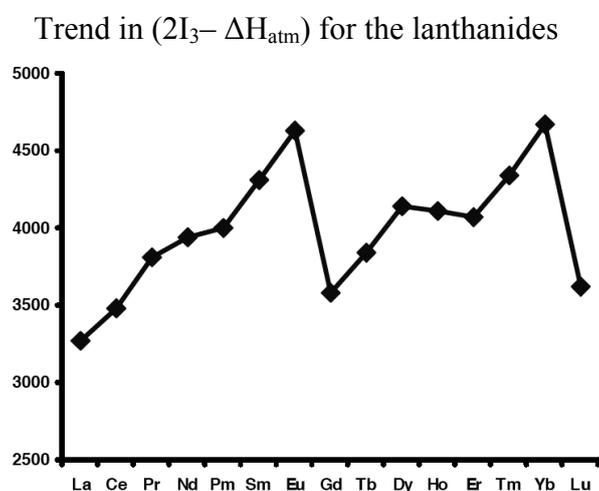
8. Answer **all** parts.

(i) For the reaction



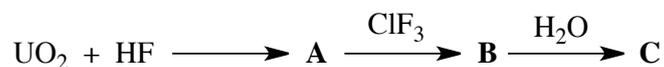
Construct a thermodynamic cycle for this reaction in terms of lattice enthalpies L , ionisation energies I_1 , I_2 and I_3 , and heats of atomisation ΔH_{atm} . [3]

(ii) Given that I_1 and I_2 change linearly across the lanthanide series, use the diagram below to discuss the stabilities of the divalent states of the lanthanides. [6]



(iii) Comment on the observation that, despite its low I_3 , lanthanum forms compounds such as LaI_2 and LaS . [3]

(iv) Identify compounds **A**, **B** and **C** in the reaction sequence below and comment on the structure, bonding and properties of **B** and **C** in light of the data provided. [8]



A and **C** have formula weights of 314 and 308 respectively.

B has a boiling point of 56°C .

The infrared spectrum of **C** shows a strong band at $\sim 950\text{ cm}^{-1}$ which is shifted if $^{18}\text{OH}_2$ is used in the reaction with **B**. This band also persists when **C** is dissolved in strong acid or alkali.

[Relative atomic masses: U 238, O 16, F 19]

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