University of Canterbury

End of Year Examinations 2005

Prescription Number(s):	CHEM 321
Paper Title:	Inorganic & Structural Chemistry

Time Allowed:	THREE HOURS
Number of pages:	EIGHT

Answer **SIX** questions.

All questions are of equal value.

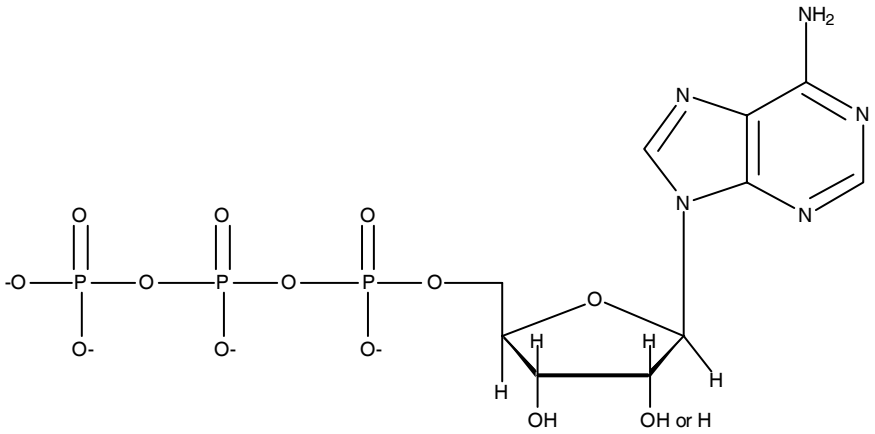
TURN OVER

1. (a)Describe the kind of reaction that is catalysed by vitamin B12 dependent enzymes. How is the vitamin B12 involved?

   (b) Describe how the cobalt-carbon bond energy is determined for vitamin B12. How does the bond energy differ between free vitamin B12 and the enzyme-bound form? What theories have been put forward to account for the difference in bond energy in the free and enzyme-bound forms? What evidence has been put forward in support of these theories?

2. (a) Describe the ways that metal ions and their compounds can bind to DNA.

   (b) ATP and its deoxy form are very important biological molecules, which are involved in, among other things, phosphorylation reactions and DNA synthesis. Describe how the presence and location of metal ions can affect the kind of chemistry that is observed.



ATP

   (c) Outline the Fenton reaction, and describe how and why it can be used to determine the site on a DNA molecule at which a DNA binding molecule is bound.

3. (a) (10 marks)

(i) The principal site of DNA reactivity towards the anti-cancer drug cisplatin is adjacent GG bases. How is the drug believed to find this site? What experimental evidence supports this hypothesis?

(ii) Why does the *trans* isomer not exhibit similar anticancer properties? In spite of this the *trans* isomer is a potentially useful drug in cancer treatment. Why?

(b) (10 marks)

(i) Discuss the difficulties that are encountered in applying a *systems engineering* approach to improving the sustainability and the environmental impact of industrial operations.

(ii) Describe, with the aid of a simple flowsheet, the unit operations involved in the large scale recovery of zinc from sulfidic ores by the conventional hydrometallurgy-based process. Indicate the main environmental concerns associated with the operation of this process.

4. (a) (7 marks)

Use the thermodynamic data below to calculate the temperature above which it is thermodynamically feasible to reduce chromia (Cr_2O_3) to chromium metal with carbon. Assume that changes in heat capacities for the reactions are negligible and that standard conditions (other than temperature) apply.

	ΔH_f^o/kJ mol^{-1}	S^o/J K^{-1} mol^{-1}
C(graphite)	0	5.74
CO(g)	-110.53	197.67
Cr(s)	0	23.77
Cr_2O_3(s)	-1139.70	81.20

Question 4 continued on following page

Question 4 continued

(b) An Ellingham diagram for some oxides is given below.

(i) (2 marks)

If an alloy of magnesium and aluminium were heated in limited oxygen at 500^{o}C, which metal should be preferentially oxidized?

(ii) (2 marks)

Comment on the shape of the H_2O plot (shown as the dashed line).

(iii) (3 marks)

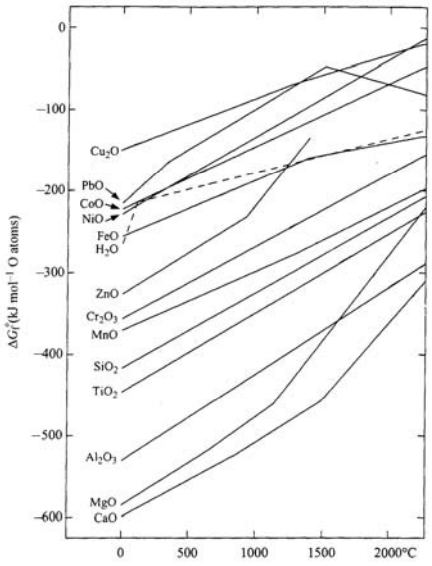
Indicate, with reasons, whether nickel or aluminium is the more appropriate material for the construction of steam pipes.

(iv) (3 marks)

Indicate, with reasons, whether MgO or SiO_2 is the more appropriate material for the construction of crucibles for molten aluminium.

(v) (3 marks)

Suggest conditions under which it would be possible to operate a process to reduce Cr_2O_3 to chromium metal with hydrogen.



5. Answer **SEVEN** questions from (a) – (j).

(a) What is the **lattice** of a structure and how does a **unit cell** relate to a lattice?

(b) $P2_1/c$ is a space-group symbol. Explain what each character of the symbol means.

(c) Crystal systems can have certain types of symmetry elements not possible in single finite molecules. Describe, with diagrams if necessary, these types.

(d) What is a **structure factor** and how is it related to the intensity of a diffracted X-ray beam?

(e) If the intensity of the diffracted beam is proportional to the size of the crystal, why are huge crystals not used in single crystal X-ray crystallography?

(f) Define **"atomic scattering factor".**

(g) Why are X-rays, rather than other forms of electromagnetic radiation, used for the determination of structures by diffraction methods?

(h) What is a Patterson synthesis and when is it most applicable in solving a crystal structure?

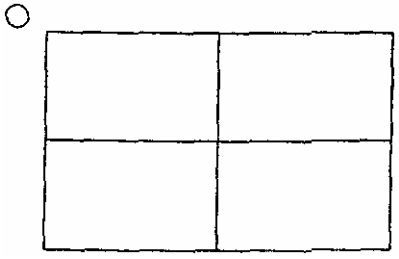
(i) X-ray intensity data are often collected at -110°C rather than at room temperature. Why?

(j) What is an **asymmetric unit** and how does it differ, if at all, from a **unit cell**?

6. (a) (10 marks)

Consider plane group *p2mg* shown below.

Rectangular *2mm* *No. 7 p2mg*

(I) 

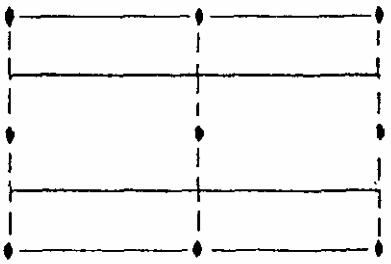
(II) 

Diagram (I) has been cleared of all information except a starting position. Diagram (II) shows the symmetry elements of this plane group.

(i) In your answer booklet, using a copy of (I), show all the equivalent positions generated by the symmetry elements in (II).

(ii) Explain each of the symmetry elements in (II) and describe how each position you have drawn was generated by one of these.

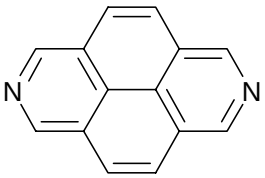
(b) (10 marks)

Describe the types of stereoisomers that can exist in mononuclear and binuclear octahedral transition-metal complexes. Explain why attention must be paid to the possibility of isomerism when attempting to prepare metallosupramolecular assemblies.

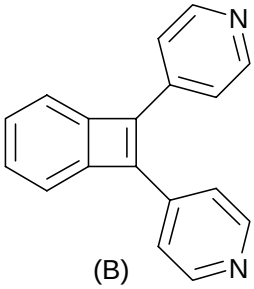
7. (a) What is metallosupramolecular chemistry?

(b) Outline two approaches that can be used to self-assemble molecular squares using transition metals and bridging ligands, and explain how the sizes of the squares can be controlled.

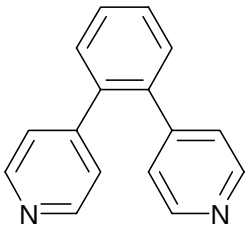
(c) Shown below are four ligands (A)-(D) and two palladium reactants (E), (F) (where X is a readily displaced labile ligand). What types of self-assembled structures would you expect as a result of mixing (E) with each of (A)-(D)? What structures would form from reacting (F) with (A) and with (B)? (It is not necessary to draw the full molecular structures).



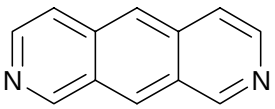
(A)



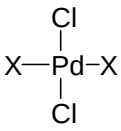
(B)



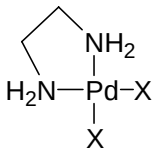
(C)



(D)



(E)



(F)

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