

**Ollscoil na hÉireann, Gaillimh**  
***National University of Ireland, Galway***

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**SUMMER EXAMINATIONS, 2002**

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**SECOND SCIENCE CHEMISTRY**

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**Inorganic Chemistry CH-204**

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Time allowed: *Two* hours

(Answer *four* questions)

1. 0.21 g of a hydrated salt of composition  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  was dissolved in  $500 \text{ cm}^3$  of distilled water (Solution A).  $50 \text{ cm}^3$  of solution A were titrated with  $0.012 \text{ mol dm}^{-3}$  EDTA solution to an Erio-T endpoint (endpoint =  $8.3 \text{ cm}^3$ ).

Answer each of the following:

- |  |            |
|--|------------|
| (a) Draw the structure of EDTA   | [3 marks]  |
| (b) Calculate the number of moles of Mg in $50 \text{ cm}^3$ of solution A             | [5 marks]. |
| (c) Calculate the number of moles of Mg in $500 \text{ cm}^3$ of solution A            | [3 marks]. |
| (d) Calculate the relative molecular mass of $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ | [8 marks]. |
| (e) Calculate the value of x in $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$              | [6 marks]. |
2. Contrast the chemistry of the Group 1 and Group 2 under the following headings
- |   |            |
|---|------------|
| (a) Reaction with water                   | [8 marks]  |
| (b) Complex formation                     | [10 marks] |
| (c) Solubility of fluorides and sulfates. | [7 marks]  |

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3. Answer (a) and (b).

- (a) Explain the fall in single bond energy along the series C-C, N-N, O-O and F-F. [13 marks]
- (b) Give a short description (with some examples) of the diagonal relationships shown by Li/Mg, Be/Al and B/Si. [12 Marks]

4. Answer (a) and (b).

- (a) Use the LCAO method to derive energy level diagrams for  $\text{Li}_2$  and  $\text{O}_2$ . Using your diagrams predict some of the properties of the  $\text{Li}_2$  and  $\text{O}_2$  molecules. [13 marks]
- (b) Use the valence shell electron pair repulsion theory to derive structures for the following;  $\text{SeCl}_4$ ,  $\text{XeO}_4$ ,  $\text{BrF}_2\text{O}^+$ ,  $\text{BrFO}_3$ ,  $\text{IF}_5$  and  $[\text{ICl}_4]^-$ . [12 marks]

5. Illustrate each of the following:

- (a) a coordination compound of  $\text{Co}^{3+}$  which is paramagnetic.
- (b) a coordination compound of  $\text{Co}^{3+}$  which is diamagnetic.
- (c) the ligand dibenzo-14-crown-4 coordinated to a  $\text{Ni}^{2+}$  ion.
- (d) *cis* and *trans* isomers of a square-planar coordination compound.
- (e) an optically active octahedral coordination compound.
- (f) a Lewis base.
- (g) the reaction of aqueous nickel(II) chloride with ammonia.
- (h) the *mer* and *fac* isomers of a coordination compound.
- (i) a porphyrin ligand coordinated to an  $\text{Fe}^{3+}$  ion.
- (j) a hexadentate ligand coordinated to a magnesium ion.

[2.5 marks each part]

6. Answer each of the following:

- (a) Describe the crystal field splitting pattern for octahedral complexes of transition metal ions. [6 marks]
- (b) Briefly explain why compounds of first row transition metals are coloured. [6 marks]
- (c) Write a short note on the spectrochemical series and place the ligands ammonia, cyanide, chloride, and water in the order that they occur in the spectrochemical series. [5 marks]
- (d) Predict the magnetic moments of the following compounds.  
 $[\text{Ti}(\text{CN})_6]^{3-}$ ;  $[\text{CoCl}_6]^{3-}$ ;  $[\text{Cr}(\text{CN})_6]^{4-}$ ;  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  [8marks]

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7. Answer (a), (b) and (c).

- (a) Clearly show, with the aid of diagrams, how two types of tetrahedral sites are developed between every two close packed layers of atoms and further explain why each type adopts a true close packed arrangement. Finally, show the stacking sequence of tetrahedral sites in both hexagonal and cubic close packing.
- (b) With the aid of diagrams of the unit cells, show the manner in which half of the tetrahedral sites are occupied in the zinc-blende and wurtzite structures. Clearly show that the occupied tetrahedral sites in the wurtzite structure adopt a hexagonal close packed array whereas the occupied tetrahedral sites in the zinc-blende structure adopt a cubic close packed array.
- (c) Describe, with the aid of diagrams, the structures of CuAu and ZnCu ( $\beta$ -brass).

8. Account as fully as possible for five of the following (where appropriate provide chemical equations or structural formulae; the equations need not necessarily be balanced).

- (a) Both the iron and oxalate content of  $\text{Fe(oxalate).nH}_2\text{O}$  can be determined by permanganate titration.
- (b) When an aqueous basic solution of potassium chromate is acidified with HCl, a colour change to a golden yellow takes place but chlorine gas is not produced. When zinc metal is added to the acidified solution further colour changes to green and eventually to blue take place and if the zinc is removed the colour reverts to green but not to the original golden yellow.
- (c) When iodide is added to an acidic aqueous copper(II) sulphate solution, a grayish white precipitate is formed in a dark brown coloured solution. On the other hand, if NaOH is added to the original solution, a bluish green precipitate is obtained and this precipitate re-dissolves to give an intensely blue coloured solution if a large excess of ammonium hydroxide is further added.
- (d) Hardness in water can be classified as either permanent or temporary and both can be determined readily by titration.
- (e) The Ni(II) content of a solution can be determined gravimetrically.
- (f) The total content of iron in an aqueous solution containing both Fe(II) and Fe(III) can be determined by a procedure which employs thiocyanate ( $\text{NCS}^-$ ) in a Beer's law type application. However, the determination must be carried out under strongly acidic conditions, avoiding the use of sulphuric acid.
- (g) An acidic permanganate solution reacts with both iodide and chloride. In the case of chloride addition, a colour change from pink to colourless takes place. Addition of sodium hydroxide to the colourless solution results in the formation of a white precipitate which darkens on exposure to the atmosphere.
- (h)  $\text{Fe}_2(\text{CO})_9$  exhibits two carbonyl related frequencies in its infrared spectrum whereas  $\text{Mo(CO)}_6$  exhibits only one such vibration. Neither complex exhibits an infrared band in the range  $2500 - 3500 \text{ cm}^{-1}$  region of the spectrum; in that respect their spectra are different to that of  $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ .