

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS, 1999

SECOND SCIENCE CHEMISTRY

Second Paper

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Time allowed: *Two* hours

(Answer *four* questions)

25 cm³ of solution, A, containing CuSO₄ was passed over a column of Zerolit 225 in the hydrogen form. The sulphuric acid raffinate was collected and diluted to 250 cm³ with distilled water (Solution B).

25 cm³ of solution B was titrated with 0.05 mol dm⁻³ NaOH (endpoint = 10.00 cm³).

The copper was now displaced from the column using 2 mol dm⁻³ HCl and the raffinate was diluted to 250 cm³ with distilled water (Solution C).

A 25 cm³ aliquot of solution C was neutralised to pH 4.5, 1 g of KI was added following which the liberated iodine was titrated to a starch endpoint with 0.05 mol dm⁻³ Na₂S₂O₃ (endpoint = x cm³).

Draw a flow-diagram outlining the procedures in the analysis.

Using the titration data, calculate:

- (a) The sulphate concentration (g dm⁻³) in solution B.
- (b) The sulphate concentration (g dm⁻³) in solution A.
- (c) The value of x in the thiosulfate titration.

Equation: $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaI} + \text{Na}_4\text{S}_4\text{O}_6$
RMM: S, 32.06, O, 16.00, Cu, 63.55.

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2. Answer (a) and (b)

- (a) Suggest reasons why carbon forms more stable compounds with bonds to itself than any other element.
- (b) Describe briefly the synthesis of the silicones.

3. Answer (a) and (b).

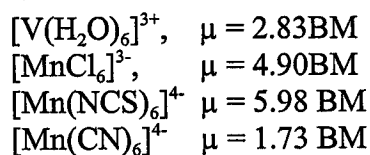
- (a) Compare the chemistry of nitrogen and phosphorus. Include a discussion of valence and bond type in your answer.
- (b) What are the structures adopted by P_4O_6 and P_4O_{10} ? What are the simplest oxy-acids formed on hydrolysis of P_4O_6 and P_4O_{10} ?

4. Answer (a) and (b).

- (a) Use the LCAO method to derive bond orders for the following O_2 , O_2^+ , O_2^- , O_2^{2-} and NO^+ .
- (b) Use the valence shell electron pair repulsion theory to derive structures for the following; SF_4 , SF_6 , $SOCl_2$, ClF_3 , IF_5 and $[ICl_4]^-$.

5. Answer each of the following:

- (a) Explain the origin of paramagnetism and diamagnetism.
- (b) Explain why the d-orbitals in octahedral coordination compounds of the first row transition metals split into t_{2g} and e_g sets.
- (c) Using d-orbital splitting, account for the magnetic moments of the following complex ions;



6. Answer each of the following;

- (a) Sketch the complex ion $[Cr(edta)]^-$, where edta is the ethylenediaminetetraacetate anion.
- (b) Sketch the complex ion, $[Ce(NO_3)_6]^{2-}$, and give its coordination number.
- (c) Sketch all isomers of the complex ion $[CrCl_2(ox)_2]^{3-}$, where ox is the oxalate anion.
- (d) Sketch all isomers of $IrCl_3(CO)(PPh_3)_2$.
- (e) The complex ion $[CoNO_2(NH_3)_5]^{2+}$ exists in red and yellow forms. Sketch the molecular structure for the possible forms.

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7. Answer (a) and (b).

- (a) Outline the principles of close packing of spheres. Clearly explain how tetrahedral and octahedral sites are generated and why a distinction can be made between two types of tetrahedral sites. Indicate how all types of interstitial sites are distributed within true close packed arrangements.
- (b) Draw the unit cell of hexagonal close packing and explain fully why six spheres can be considered as making full contributions to the unit cell. Show the positions of octahedral and tetrahedral sites and show how half of the tetrahedral sites are occupied in the wurtzite (ZnS) structure. Compare this structure with the zinc blende structure.

8. Explain *five* of the following

- (a) $\text{Fe}_2(\text{CO})_9$ exhibits carbonyl stretching frequencies in two regions of its infrared spectrum whereas $\text{Mo}(\text{CO})_6$ exhibits CO stretch band.
- (b) The infrared active cyanide stretching frequencies are different for $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. Furthermore, a strong absorption appears above 3000 cm^{-1} in the infrared spectrum of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ whereas no such absorption is observed in the infrared spectrum of $\text{K}_3\text{Fe}(\text{CN})_6$.
- (c) It is possible to separate zinc and magnesium using an anion exchange resin.
- (d) When a basic aqueous solution of potassium chromate is acidified a colour change is observed.
- (e) When HCl is added to an aqueous potassium permanganate solution a colour change is observed but no such colour change is observed when sulphuric acid is employed.
- (f) Addition of potassium iodide to a basic aqueous permanganate solution results initially in the formation of a green colour which finally gives way to a black precipitate.
- (g) Addition of sodium hydroxide to an aqueous copper sulphate solution results in the formation of a bluish green precipitate whereas the addition of an excess of ammonium hydroxide results in the formation of a deep blue solution.
- (h) Addition of potassium iodide to an aqueous solution of FeCl_3 results in a reaction which does not take place if the FeCl_3 solution also contains dissolved phosphate.

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