

**NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY**  
**DEPARTMENT OF APPLIED CHEMISTRY**  
**END OF SEMESTER EXAMINATIONS – JANUARY 2004**  
**ANALYTICAL CHEMISTRY II - SCH 2106**  
**TIME – 3 HRS**

**INSTRUCTION TO CANDIDATES**

Answer **ALL** questions from Section A and **ANY THREE** from Section B  
 Section A carries 40 marks and Section B carries 60 marks  
 Total Marks – 100

**SECTION A**

1. (a) Describe the alkaline error in the measurement of pH. Under what circumstances is this error appreciable? How are pH data affected by alkaline error? [6 marks]
- (b) How does a gas-sensing probe differ from other membrane electrodes. [4 marks]
2. (a) The solubility product constant for  $\text{Ag}_2\text{SO}_3$  is  $1.5 \times 10^{-4}$ . Calculate  $E^0$  for the process  

$$\text{Ag}_2\text{SO}_3(\text{s}) + 2\text{e}^- \leftrightarrow 2\text{Ag}(\text{s}) + \text{SO}_3^{2-}$$
 [5 marks]
- (b) Write balanced net-ionic equations for the following reactions.
  - (i)  $\text{MnO}_4^- + \text{VO}^{2+} \rightarrow \text{Mn}^{2+} + \text{V}(\text{OH})_4^+$  [2 marks]
  - (ii)  $\text{Cr}_2\text{O}_7^{2-} + \text{U}^{4+} \rightarrow \text{Cr}^{3+} + \text{UO}_2^{2+}$  [2 marks]
  - (iii)  $\text{IO}_3^- + \text{I}^- \rightarrow \text{I}_2(\text{aq})$  [2 marks]
3. The equilibrium constant for the conjugate acid/base pair  

$$\text{HIn} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{In}^-$$
 is  $8.00 \times 10^{-5}$ . From the additional information

Species	Absorption Maximum, nm	Molar Absorptivity	
		430 nm	600 nm
HIn	430	$8.04 \times 10^3$	$1.23 \times 10^3$
In <sup>-</sup>	600	$0.775 \times 10^3$	$6.96 \times 10^3$

Calculate the absorbance at 430 nm and 600 nm for the following indicator concentrations:  $3.00 \times 10^{-4}$ ,  $0.25 \times 10^{-4}$ ,  $0.500 \times 10^{-4}$  [10 marks]

4. In a hydrogen/oxygen flame, an atomic absorption peak for iron decreases in the presence of large concentrations of sulfate ion.

(a) Suggest an explanation for this observation [2 marks]

(b) Suggest three possible methods for overcoming the potential interference of sulfate in a quantitative determination of iron. [3 marks]

(c) Why is spectrofluorometry potentially more sensitive than spectrophotometry? [4 marks]

### **SECTION B**

5. (a) With the aid of clearly labelled diagrams and appropriate equations, describe different types of ion-selective electrodes in terms of:

(i) the construction of the electrodes [5 marks]

(ii) differences in the response mechanisms [5 marks]

(iii) applications [5 marks]

(b) What do you understand by residual current in polarography? Explain its causes. [5 marks]

6. Silver is to be deposited from a solution that is 0.150 M in  $\text{Ag}(\text{CN})_2^-$ , 0.320 M in KCN, and buffered to a pH of 10.00. Oxygen is evolved at the anode at a partial pressure of 1.00 atm. The cell has a resistance of 2.90  $\Omega$ ; the temperature is 25°C.

Calculate:

(i) the theoretical potential needed to initiate deposition of silver from this solution. [5 marks]

(ii) the IR drop associated with a current of 0.12 A. [5 marks]

(iii) the initial applied potential, given that the  $\text{O}_2$  overvoltage is 0.80 V. [5 marks]

(iv) the applied potential when  $[\text{Ag}(\text{CN})_2^-]$  is  $1.00 \times 10^{-5}$  M, assuming no changes in IR drop and  $\text{O}_2$  overpotential. [5 marks]

7. (a) With the aid of a clearly labelled diagram describe in details the relaxation pathways that could be followed by an excited molecule when returning to its ground state, as a way of losing excess energy. [10 marks]
- (b) Briefly define:
- (i) Stoke shifts [2 marks]
  - (ii) Resonance fluorescence [2 marks]
- (c) The quantum efficiency of fluorene is approximately 1.0 while that of biphenyl is about 0.2. With the aid of the structural formulae of these compounds explain the statement. [6 marks]
8. (a) Draw a labelled diagram of a hollow cathode lamp. [5 marks]
- (b) Distinguish between Doppler broadening and pressure broadening. [5 marks]
- (c) A 5.00 ml sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation, the resulting solution was brought to pH 3 and extracted with two 5 ml portions of methyl isobutyl ketone containing the organic lead-complexing agent APCD. The extract was aspirated directly into an air/acetylene flame and yielded an absorbance of 0.502 at 283.3 nm. 5.00 ml aliquots of standard solutions containing 0.400 and 0.600 ppm of lead were treated in the same way and yielded absorbances of 0.396 and 0.599. Calculate the parts per million of lead in the sample assuming that Beer's law is followed. [10 marks]

**END OF QUESTION PAPER!!!**