

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
SUPPLEMENTARY EXAMINATIONS – JULY 2003
ANALYTICAL CHEMISTRY II - SCH 2106
TIME – 3 HRS

INSTRUCTION TO CANDIDATES

Answer All Questions
Total Marks – 100

1. (a) Describe in detail the errors that affect pH measurements with the glass electrode. (8 marks)
- (b) What is the operational definition of pH? Why is it used? (5 marks)
- (c) (i) Calculate the standard potential for the reaction;
 $\text{CuBr(s)} + e \rightleftharpoons \text{Cu(s)} + \text{Br}$
For CuBr, $K_{sp} = 5.2 \times 10^{-9}$ (4 marks)
- (ii) Give a schematic representation of a cell with a copper indicator electrode as an anode and a saturated calomel electrode as a cathode that could be used for the determination of Br. (2 marks)
- (iii) Derive an equation that relates the measured potential of the cell in (ii) to pBr (assume that the junction potential is zero). (3 marks)
- (iv) Calculate the pBr of a bromide containing solution that is saturated with CuBr and contained in the cell described in (ii) if the resulting potential is -0.071V. (3 marks)
2. (a) Describe in detail the transitions responsible for absorption by:
- (i) Lanthanide and actinide ions (5 marks)
- (ii) Elements of the first and second transition-metal series. (10 marks)

2. (b) What is charge-transfer absorption? Give examples in your answer. (10 marks)
3. (a) Define the following terms:
- (i) resonance fluorescence (2 marks)
 - (ii) internal conversion (2 marks)
 - (iii) Stoke shift (2 marks)
 - (iv) quantum yield (2 marks)
- (b) Why do some absorbing compounds fluoresce and others not? (4 marks)
- (c) Explain how structural rigidity, temperature and solvents affect fluorescence. (10 marks)
- (d) Why are most fluorescence instruments double beam in design? (3 marks)
4. (a) A 40.00mL aliquot of 0.050M HNO_2 is diluted to 75.00ml and titrated with 0.080M Ce^{4+} . The pH of the solution is maintained at 1.00 throughout the titration; the formal potential of the cerium system is 1.44V.
- (i) Calculate the potential of the indicator electrode with respect to a saturated calomel reference electrode after the addition of 5.00, 10.00, 15.00, 25.00, 40.00, 49.00, 50.00, 51.00 and 60.00mL of cerium(IV). (15 marks)
 - (ii) Draw a titration curve for these data. (10 marks)

END OF QUESTION PAPER!!!