

八十四學年度 原子科學研究所 乙 組碩士班研究生入學考試

科目 分析化學 科號 3202 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

1. a). Calculate the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl . The base dissociation constant for NH_3 is 1.76×10^{-5} .
 b). Calculate the pH change that takes place when a 100-ml portion of 0.0500 M HCl is added to 400-ml of the buffer solution described in a). (12%)

2. Calculate the potential of the cell
 $\text{SEC} \parallel \text{aqueous solution} \mid \text{Hg}$
 when the aqueous solution is
 a). 7.4×10^{-3} M Hg^{2+}
 b). Hg^{2+} (2.00×10^{-3} M), OAc^- (0.100 M)
 $[\text{Hg}^{2+} + 2\text{OAc}^- \rightleftharpoons \text{Hg}(\text{OAc})_2(\text{aq}) \quad K_f = 2.7 \times 10^8]$
 The respective electrode potentials are
 SEC (saturated calomel electrode) 0.244 V at 25°C, and
 $\text{Hg}^{2+} + 2e^- \rightleftharpoons 2\text{Hg}(l) \quad E^\circ = -0.854 \text{ V}$ (12%)

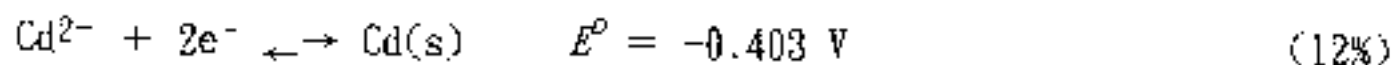
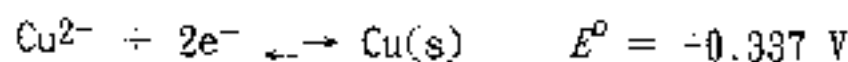
3. Manganese is often determined spectrophotometrically as the permanganate ion (MnO_4^-) whose aqueous solutions are a deep purple color ($\lambda_{\text{max}} = 525 \text{ nm}$). A 1.00×10^{-4} M solution of KMnO_4 gives an absorbance of 0.585 when a 1.00 centimeter cell is used at 525 nm. A 0.500 gram sample of a manganese-containing alloy is dissolved in acid, and all the manganese is converted to MnO_4^- by periodate oxidation. The sample is then diluted to 500 milliliters in a volumetric flask, and its absorbance, taken at 525 nanometers in a 1.00 centimeter cell, is found to be 0.400. Assume that the permanganate system follows Beer's law and calculate the weight percent of manganese in the unknown. (At. Wt. of Mn = 54.94) (12%)

4. Consider a cell consisting of a copper electrode in contact with 1.00 M Cu^{2+} , a cadmium electrode in contact with 1.00 M Cd^{2+} , and a connecting salt bridge. The cell has a resistance of 4.00 Ω .
 a). Calculate the potential needed to develop a current of 0.0200 A in the electrolytic cell
 $\text{Cu} \mid \text{Cu}^{2+}(1.00 \text{ M}) \parallel \text{Cd}^{2+}(1.00 \text{ M}) \mid \text{Cd}$
 b). Calculate the cell potential when there is a current of 0.0200 A in the galvanic cell
 $\text{Cd} \mid \text{Cd}^{2+}(1.00 \text{ M}) \parallel \text{Cu}^{2+}(1.00 \text{ M}) \mid \text{Cu}$

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The standard electrode potentials are



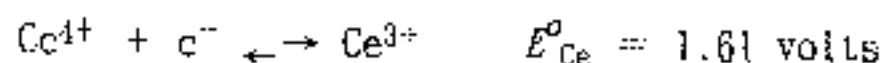
5. Calculate the solubility of $\text{Fe}(\text{OH})_3$ in water.

$$[\text{Fe}^{3+}] [\text{OH}^{-}]^3 = 4 \times 10^{-38}$$

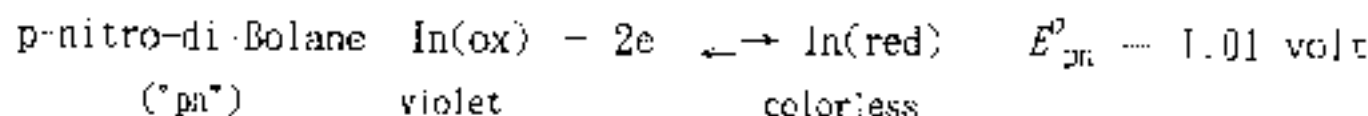
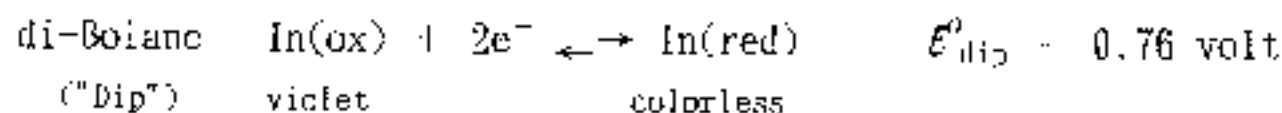
$$[\text{H}_3\text{O}^{+}] [\text{OH}^{-}] = 1.00 \times 10^{-14}$$

Note: the validity of assumption should be checked in order to avoid a faulty result. (12%)

6. There has been much discussion of the titration of Fe^{2+} with Ce^{4+} . Under the conditions of this problem, the E° values for the half reactions of Fe and Ce are as given as follows



The endpoint solution potential for a titration of Fe^{2+} by Ce^{4+} is found to be 1.19 volts. It would be nice to detect the endpoint with an indicator. Two new indicators are



Assume that, for either indicator, the color change from colorless to violet is visible when $[\text{In(ox)}] / [\text{In(red)}] = 10$. Would either, or both indicators be suitable for the Fe^{2+} - Ce^{4+} titration? Explain in your reason. (10%)

7. Predict the order of elution of

i). n-hexane, n-hexanol, benzene

ii). ethyl acetate, diethyl ether, nitrobutane

for a) a normal-phase separation, and b) a reversed-phase separation.

(10%)

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8. Describe and compare the differences between the following terms:
- a). Sensitivity / Detection limit
 - b). Population standard deviation (σ) / Sample standard deviation (s)
 - c). Conjugate acid / Conjugate base
 - d). Concentration polarization / Kinetic polarization
 - e). Adsorption chromatography / Partition chromatography
 - f). Isocratic elution / Gradient elution
- (20%)