國 立 清 華 大 學 命 題 紙

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
   SEC || aqueous solution | 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)
   [$Hg^{2+} + 2OAc^- \rightleftarrows Hg(OAc)_2(aq)$ $K_f=2.7\times10^{8}$]
   The respective electrode potentials are
   SEC (saturated calomel electrode) 0.244 V at 25°C, and
   $Hg^{2+} + 2e^- \rightleftarrows 2Hg(l)$ $E^\circ = +0.854$ V (12%)

3. Manganese is often determined spectrophotometrically as the permanganate ion (MnO_4^-) whose aqueous solutions are a deep purple color (λ_{max} = 525 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
   Cu | Cu^{2+}(1.00 M) || Cd^{2+}(1.00 M) | Cd
   b). Calculate the cell potential when there is a current of 0.0200 A in the galvanic cell
   Cd | Cd^{2+}(1.00 M) || Cu^{2+}(1.00 M) | Cu

The standard electrode potentials are

$Cu^{2-} + 2e^- \rightleftarrows Cu(s)$ $\quad E^o = +0.337$ V

$Cd^{2-} + 2e^- \rightleftarrows Cd(s)$ $\quad E^o = -0.403$ V (12%)

5. Calculate the solubility of $Fe(OH)_3$ in water.

$[Fe^{3-}]\,[OH^-]^3 = 4\times10^{-38}$

$[H_3O^+]\,[OH^-] = 1.00\times10^{-14}$

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^o values for the half reactions of Fe and Ce are as given as follows

$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ $\quad E^o_{Fe} = 0.77$ volts

$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$ $\quad E^o_{Ce} = 1.61$ volts

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

di-Bolane ("Dip") $\quad In(ox) + 2e^- \rightleftarrows In(red)$ $\quad E^o_{dip} = 0.76$ volt

violet — colorless

p-nitro-di-Bolane ("pn") $\quad In(ox) - 2e \rightleftarrows In(red)$ $\quad E^o_{pn} = 1.01$ volt

violet — colorless

Assume that, for either indicator, the color change from colorless to violet is visible when $[In(ox)] / [In(red)] = 10$. Would either, or both indicators be suibable 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. Discribe and compare the differences between the following terms:
   a). Sensitivity / Detection limit
   b). Population standard derviation (σ) / Sample standard derviation(s)
   c). Conjugate acid / Conjugate base
   d). Concentration polarization / Kinetic polarization
   e). Adsorption chromatography / Partition chromatography
   f). Isocratic elution / Gradient elution (20%)