題號: 59

## 國立臺灣大學 111 學年度碩士班招生考試試題

科目: 分析化學(B)

題號:59

共2頁之第1頁

#### Attentions:

節次:

- a) <u>Do not</u> leave your answers in the table on the first page of the answer booklet. Write all your answers in the second and subsequent pages of the answer booklet.
- b) Answers should appear in order in the answer booklet. Each answer should be preceded with its question number/code. Answers not preceded with question numbers/codes will not be credited.
- c) Pay attention to the sign and unit of your answers.
- d) The following values may be of some use: exp(1.00) = 2.718; exp(2.00) = 7.389; exp(3.00) = 20.09; exp(5.00) = 148.4; exp(5
- 1.(9%) (a) A 15.0 mL of a 0.400 M NaOH solution is needed to completely neutralize 20.0 mL of a H<sub>2</sub>SO<sub>4</sub> solution. What is the concentration of the H<sub>2</sub>SO<sub>4</sub> solution?

(b) Predict the pH at the equivalence point if NaOH is used to titrate the H₂SO₄ solution.

- (c) If the concentration of H<sub>2</sub>SO<sub>4</sub> solution is known and the concentration of NaOH solution is unknown, can the H<sub>2</sub>SO<sub>4</sub> solution be used to titrate the NaOH solution? Explain.
- (d) Can H<sub>2</sub>SO<sub>4</sub> solution be used to titrate NH<sub>3</sub> solution, if the concentration of the H<sub>2</sub>SO<sub>4</sub> solution is known and the concentration of the NH<sub>3</sub> solution is unknown? Explain.
- 2.(11%) The standard reduction potential table shows the following two half reactions:

Fe<sup>3+</sup> + e<sup>-</sup> 
$$\Rightarrow$$
 Fe<sup>2+</sup> E° = 0.771 V  
I<sub>3</sub> + 2e<sup>-</sup>  $\Rightarrow$  3I E° = 0.536 V

- (a) What does the symbol "o" on the right of "E" mean for the potential? Write down the detail of the meaning.
- (b) Write down the Nernst equations for the two half reactions.
- (c) Write down the chemical equation for the reaction occurring in a galvanic cell composed of the two half reactions.
- (d) Write down the equation of the cell potential expressed as a function of the concentrations of reacting species at any instant during the reaction.
- (e) What is the cell potential when the cell reaction reaches equilibrium?
- (f) Use your answers of (b) and (e) to derive the equation that relates the standard reduction potentials with the equilibrium constant of the cell reaction.
- (g) Use your derived equation to calculate the equilibrium constant of the reaction expressed in (c).
- 3.(10%) (a) Calculate the ionic strength of a mixture solution containing 0.010 M in KCl and 0.010 M in HNO<sub>2</sub>.
  - (b) Calculate the relative error in hydronium ion concentration by using concentrations instead of activities in calculating the pH of the mixture solution. (Note:  $K_a(HNO_2) = 5.0x10^{-4}$ ;  $\alpha_{K^+} = 3.3$  Å;  $\alpha_{NO_2}^- = 3.0$  Å;  $\alpha_{Cl}^- = 3.2$  Å;  $\alpha_{H^+} = 8.8$  Å)

At 25 °C:  

$$-\log \gamma_{A} = \frac{0.509 Z_{A}^{2} \sqrt{\mu}}{1 + 0.329 \alpha_{A} \sqrt{\mu}}$$

### 4.(26%) (a) Define calibration.

- (b) Almost all except two analytical methods require some type of calibration with chemical standards. (i) What are chemical standards? (ii) What is the difference between chemical standards and primary standards? Write down the requirements for the primary standard? (iii) Give an example of chemical standard and specify the analytical method in which your example of the chemical standard can be used. (iv) Write down the two analytical methods that normally do not require calibration and explain why they do not.
- (c) External standard calibration is one of the four popular types of methods used for calibrating analytical methods. (i) Name the other three types of calibration methods and describe each of these three methods (in more than 40 words each). (ii) Define external standard. (iii) What is the analyte solution condition the external standard calibration method is used? (iv) How is the external standard calibration method carried out experimentally?
- (d) The method of least squares is a popular regression analysis approach used in external standard calibration. Use an equation and describe the method in more than 60 words.
- 5.(14%) (a) Calculate the molar solubility of CuS ( $K_{sp} = 8.1 \times 10^{-37}$ ) in water
  - (b) Using the systematic approach to calculate the molar solubility of  $Cu(OH)_2$  ( $K_{sp} = 4.66x10^{-20}$ ) in water.
- 6.(30%) The TSMC (台積電) semiconductor factory at Southern Taiwan Science Park confirmed on July 30, 2021 that some of its fabrication plants were suspected to be contaminated with gases supplied by manufacturers. It is assumed that the contamination occurred in the fabrication plants' oxygen tanks. Oxygen is associated with key processes in semiconductor manufacturing, including the generation of wafer silicon oxide for current technologies and the development of crystalline oxides required for vertical integration of future technologies.
  - (a) (i) Write down the names of seven main electromagnetic radiation regions in the order of increasing wavelength. (ii) Which radiation region does NMR rely on? (iii) Which radiation region does 566 nm belong to? (iv) Give the names of two spectroscopies that operate based on absorption of electromagnetic radiation.

題號: 59

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節次: 6

題號: 59 共 2 頁之第 2 頁

(b) What is the main use of Eriochrome black T (EBT) in analytical chemistry? Describe the working principle on which EBT shows the phenomenon of its intended use in analytical chemistry.

(c) (i) Write down the equation expressing Beer's law. (ii) Name all variables and (iii) specify the unit of each variable used in the equation.

(d) A 4.00x10<sup>-4</sup> M solution of EBT has a transmittance of 2.00% when measured in a 1.00-cm cell at the wavelength of 566 nm. Calculate (i) the absorbance of this solution and (ii) the molar absorptivity of EBT.

(e) It is well known (Talanta. 1978 Sep;25(9):519-21) that dissolved oxygen in water can be determined by its oxidation of manganese(II) to manganese(III) in alkaline medium and formation of the manganese(III) ethylenediaminetetraacetic acid complex on acidification to pH 4. Assume that you are assigned by TSMC to monitor the oxygen contamination using EBT. (i) Describe, step by step, the analytical experimental process for the monitoring and (ii) state specifically how the oxygen contamination level is to be quantified.

(f) Assume that analytical methods can be roughly categorized as seven methods including four titration methods, each based on one of the four major types of chemical reaction involved, electrochemical method, spectroscopic method, and kinetic method. Except the analytical method on which (e) uses, design your own analytical approach by (i) describing, step by step, the analytical experimental process for the monitoring based on one of the rest six analytical methods and (ii) stating specifically how the oxygen contamination level is to be quantified.

# 試題隨卷繳回