

八十六學年度 原子科學 系(所) ZI 組碩士班研究生入學考試

科目 分析化學 科號 4302 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

- (10%) 1. Calculate the potential for a half-cell consisting of a copper electrode immersed in a 0.010 M Cu^{2+} solution.



- (13%) 2. The acid dissociation constants of H_2CO_3 are

$$K_1 = 4.5 \times 10^{-7} \quad (\text{p}K_1 = 6.35)$$

$$K_2 = 5.6 \times 10^{-11} \quad (\text{p}K_2 = 10.25)$$

Please answer the following questions :

(a) Which chemical forms (H_2CO_3 , HCO_3^- and CO_3^{2-}) will predominantly exist in a solution under the specific condition of

- i) $\text{pH} = 3.00$
- ii) $\text{pH} = 6.35$
- iii) $\text{pH} = 8.00$

(b) What is the pH of 0.1 M H_2CO_3 ?

(c) What is the pH of 0.1 M NaHCO_3 ?

- (13%) 3. A spark-source mass-spectrometric method for the determination of various elements in steel was tested by analyzing several National Institute of Standards and Technology (NIST) samples. The results from three of the analyses (a, b and c) are given below. Assume that the NIST analyses are correct and determine whether or not a determinate error in any of the analyses is indicated at the 95% confidence level. (determinate error means the mean value differs significantly from the NIST value)

Element	Number of Analyses	Mean % (w/w)	Relative Standard Deviation, %	NIST result % (w/w)
(a) V	8	0.090	9.7	0.096
(b) Ni	5	0.36	5.5	0.39
(c) Cu	7	0.55	7.6	0.52

VALUES OF t FOR VARIOUS LEVELS OF PROBABILITY

Degrees of Freedom	Factor for Confidence Interval				
	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59

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科目 分析化學 科號 4302 共 3 頁第 2 頁 *請在試卷【答案卷】內作答

(13%) 4. A solution is 0.10 M in $\text{Sr}(\text{NO}_3)_2$ and 0.050 M in Ca^{2+} . Solid Na_2CO_3 is added to the solution. Assume that only the dissociation equilibria are important.

(a) Which carbonate precipitates first? What is the value of $[\text{CO}_3^{2-}]$ when this happens?

(b) What is the concentration of $[\text{Sr}^{2+}]$ in the solution when CaCO_3 first begins to form?

(c) Is it possible to separate completely the two cations by this separation system?

$$K_{sp} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = 4.1 \times 10^{-10}$$

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 7.9 \times 10^{-9}$$

(13%) 5. The following data were obtained by gas-liquid chromatography on a 40-cm packed column (t_R : retention time, W : width of peak base)

Compound	t_R , min	W , min
Air	1.9	—
Methylcyclohexane	10.0	0.76
Methylcyclohexene	10.9	0.82
Toluene	13.4	1.06

Calculate

(a) an average number of plates from the data.

(b) the standard deviation for the average in (a).

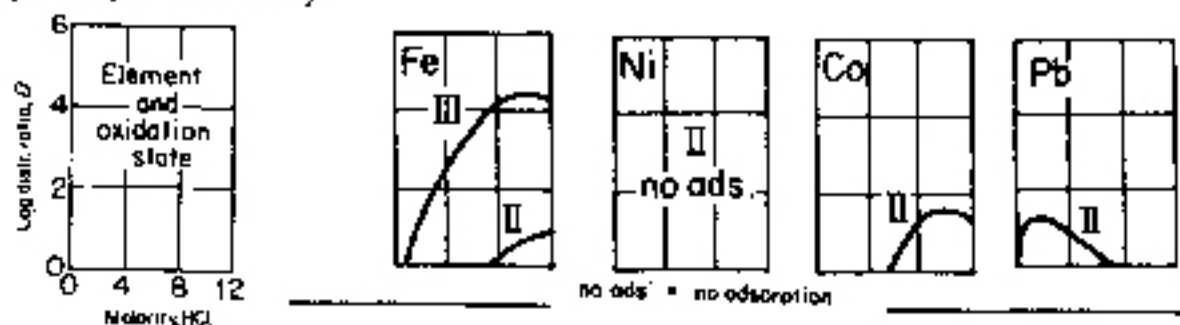
(c) an average plate height for the column.

(13%) 6. Propose separation schemes based on anion exchange chromatography for carrying out the following :

(a) separation of Fe^{2+} and Fe^{3+}

(b) separation of Ni^{2+} , Co^{2+} and Pb^{2+}

Note : The distribution ratios of the elements on Dowex-1 anion exchange resin as a function of HCl concentration, as shown below, can be used as a basis for the separation of the metal ions as chloro-complexes (such as MCl_4^-).



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- (10%) 7. Match the terms in the first list with the characteristics in the second list.
1. adsorption chromatography
 2. partition chromatography
 3. ion-exchange chromatography
 4. molecular exclusion chromatography
 5. affinity chromatography
- A. Ions in mobile phase are attracted to counter-ions covalently attached to stationary phase.
 - B. Solute in mobile phase is attracted to specific groups covalently attached to stationary phase.
 - C. Solute equilibrates between mobile phase and surface of stationary phase.
 - D. Solute equilibrates between mobile phase and film of liquid attached to stationary phase.
 - E. Different-sized solutes penetrate voids in stationary phase to different extents. Largest solutes are eluted first.
- (15%) 8. Describe the basic difference between the following spectroscopic methods of analysis:
- a) Atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS)
 - b) Flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and hydride generation atomic absorption spectrometry (HGAAS)
 - c) Inductively-coupled plasma atomic emission spectrometry (ICP-AES) and inductively-coupled plasma mass spectrometry (ICP-MS)