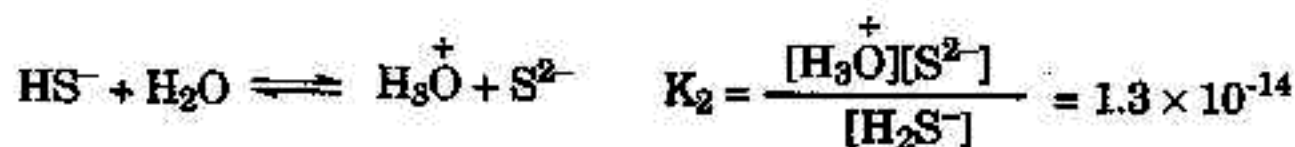
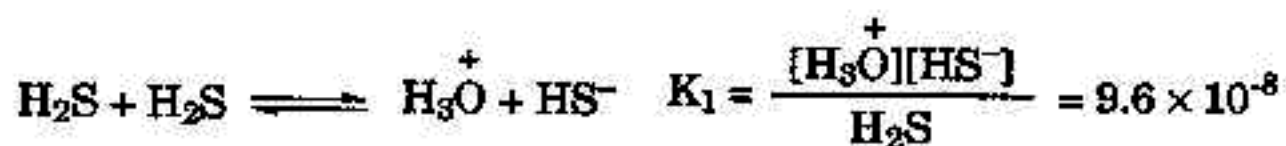


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八十八學年度 化學系 系(所) 化學、應化組碩士班研究生招生考試

科目 物理化學及分析化學 科號 0503 共 5 頁第 1 頁 *請在試卷【答案卷】內作答

- (5%) 1. Describe the preparation of 100 mL of the diluted HNO_3 acid solution with a mole ratio of one HNO_3 to three H_2O from a concentrated solution that has a specific gravity of 1.42 and is 70% HNO_3 (w/w). The specific gravity of the pure nitric acid is 1.50.
- (5%) 2. Calculate the standard deviation of the result of
$$\frac{[14.3(\pm 0.2) - 11.6(\pm 0.2)] \times 0.050(\pm 0.001)}{[8.20(\pm 10) + 1030(\pm 5)] \times 42.3(\pm 0.4)} = 1.725(\pm ?) \times 10^{-6}$$
- (5%) 3. A new procedure for the rapid determination of sulfur in kerosenes was tested on a sample known from its method of preparation to contain 0.123% S. The results were % S = 0.112, 0.118, 0.115, and 0.119. Do the data indicate that there is a bias in the method?
- (5%) 4. Find the conditions under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively with H_2S from a solution that is 0.1 M in each cation. The saturated concentration of H_2S is 0.10 M. The equilibrium constants of the relevant reactions are:

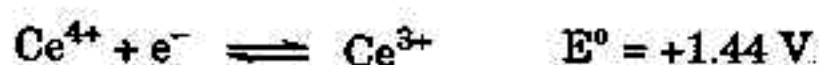


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八十八學年度 化學系 系(所) 化學、應化組碩士班研究生招生考試

科目 物理化學及分析化學 科號 0503 共 5 頁第 2 頁 *請在試卷【答案卷】內作答

- (5%) 5. Derive a titration curve for the reaction of 50.00 mL of 0.02500 M U^{4+} with 0.1000 M Ce^{4+} by adding 5.00 mL, 12.5 mL and 25.10 mL of Ce^{4+} . The solution is 1.0 M in H_2SO_4 throughout the titration (for the sake of simplicity, assume that $[H^+]$ for this solution is also about 1.0 M)



- (5%) 6. A Cell consisting of a saturated calomel electrode and a lead ion electrode developed a potential of -0.4706 V when immersed in 50.00 mL of a sample. A 5.00 mL addition of standard 0.0200 M lead solution caused the potential to shift to -0.4490 V . Calculate the molar concentration of lead in the sample.
- (5%) 7. Describe the following components of the optical instrument:
- (a) monochromator
 - (b) filter
 - (c) phototube
 - (d) photomultiplier
 - (e) photovoltaic cell
- (5%) 8. Identify factors that cause the Beer's law relationship to depart from linearity.
- (5%) 9. Substances A and B have retention times of 16.40 and 17.63 min, respectively, on a 30.0 cm column. An unretained species passes through the column in 1.30 min. The peak widths (at base) for A and B are 1.11 and 1.21 min, respectively. Calculate (a) column resolution, (b) average number of plates in the column, (c) plate height, (d) length of column required to achieve a resolution of 1.5, and (e) time required to elute substance B on the longer column.

八十八學年度 化學系 系(所) 化學、應化組碩士班研究生招生考試

科目 物理化學及分析化學 科號 0503 共 5 頁第 3 頁 *請在試卷【答案卷】內作答

(5%) 10. A GC experiment has been run to determine the optimal gas flow as shown in the following table:

Chromatogram	Gas flow (mlmin ⁻¹)	Retention time (min)	Base width (min)
A	4.0	21.0	4.0
B	3.5	23.0	4.0
C	3.0	26.5	4.0
D	2.5	32.0	4.0
E	2.0	40.0	6.0
F	1.5	44.0	8.0

- (a) Plot the HETP vs. Gas flow (V) and find the optimal gas flow. (assume the column length is 10 m)
- (b) Use the Van Deemter equation to explain the relationship between HETP and V and elaborate the each term in the Van Deemter equation.

(4%) 11. Suppose that an oscillator (with the reduced mass μ) is governed by the potential

$$V(x) = \begin{cases} \frac{k}{2} x^2 & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases}$$

- (a) What are the eigenfunctions? You only have to solve it in terms of the wavefunctions of one dimensional harmonic oscillator with the proper constraints and modifications if it is necessary.
- (b) What are the corresponding eigenvalues?

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八十八學年度 化學系 系(所) 化學、應化組碩士班研究生招生考試

科目 物理化學及分析化學 科號 0503 共 5 頁第 4 頁 *請在試卷【答案卷】內作答

(10%) 12. Briefly explain the terms or answer the following questions.

- (a) selection rule of electronic spectra
- (b) when do two operators commute?
- (c) uncertainty principle
- (d) Hund's rule
- (e) singlet state

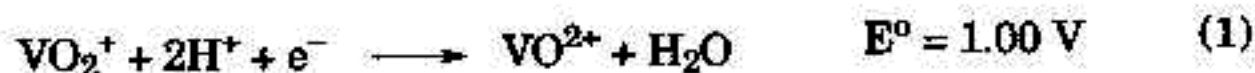
(12%) 13. Two mole of an ideal monatomic gas at 27°C and 3.0 L is allowed to expand isothermally, i.e. the temperature T is fixed, for the following two processes, (1) into an evacuated bulb, and (2) reversibly, to a total volume of 5.0 L. What are q , w , ΔE , ΔH , ΔG , and ΔS for each process?

(4%) 14. Using the relationship

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

discuss how would a system at equilibrium shift when the temperature is changed.

(10%) 15. An electrochemical cell has 0.1 M Zn^{2+} in the anodic compartment, and $[\text{VO}_2^+] = 2.0 \text{ M}$, $[\text{VO}^{2+}] = 0.01 \text{ M}$, $[\text{H}^+] = 0.5 \text{ M}$ in the cathodic compartment (see the figure shown below. Given that $T = 25^\circ\text{C}$

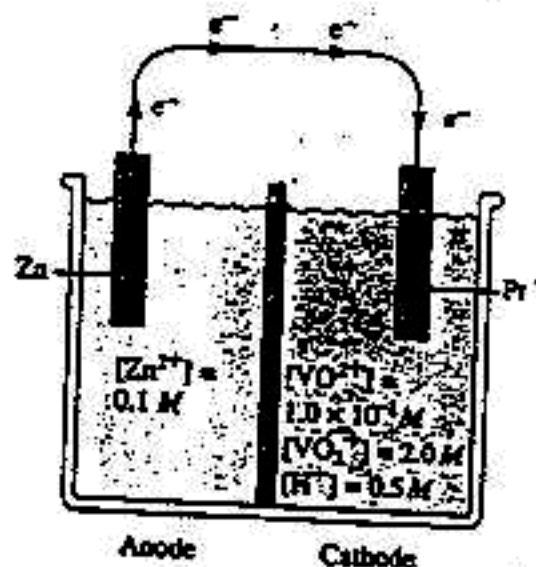


Calculate the voltage which the electrochemical cell can provide.

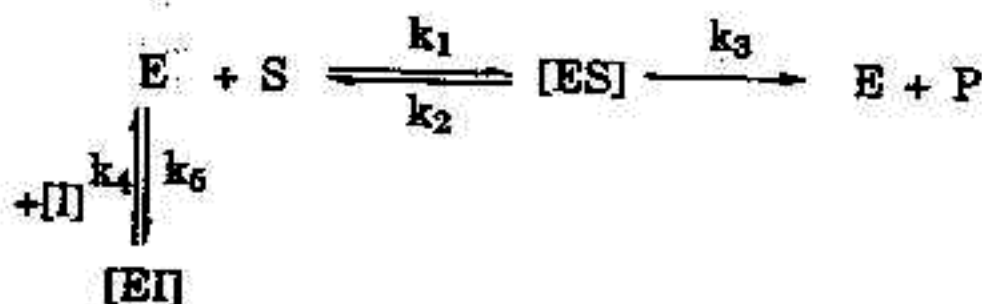
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八十八學年度 化學系 系(所) 化學、應化組碩士班研究生招生考試

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- (10%) 16. Based on the Michaelis-Menton model for noncompetitive inhibition shown below:



Show that $1/V = 1/V_{\max} + (K_M/V_{\max}) \cdot (1 + [\text{I}]/K_i) \cdot (1/[\text{S}])$,
 where $V = dP/dt$, Michaelis constant $K_M = (k_2 + k_3)/k_1$, and
 inhibition constant $K_i = k_5/k_4$.