

國立中正大學

109 學年度碩士班招生考試

試題

[第 2 節]

科目名稱	物理分析化學
系所組別	化學暨生物化學系

—作答注意事項—

※作答前請先核對「試題」、「試卷」與「准考證」之系所組別、科目名稱是否相符。

1. 預備鈴響時即可入場，但至考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。
2. 考試開始鈴響時，即可開始作答；考試結束鈴響畢，應即停止作答。
3. 入場後於考試開始 40 分鐘內不得離場。
4. 全部答題均須在試卷（答案卷）作答區內完成。
5. 試卷作答限用藍色或黑色筆（含鉛筆）書寫。
6. 試題須隨試卷繳還。



「分析化學」部分

I. 選擇題 (單選題) 每題 2 分

1. Write each answer with the correct number of significant figures:

$$3.8 + 0.040 + 7.33 = X$$

$$(26 \times 3.32) \div 100 = Y$$

$$3.432 \times 10^6 + 6.512 \times 10^4 - 1.227 \times 10^5 = Z$$

- (A) $X = 11, Y = 0.86, Z = 3.37 \times 10^6$
(B) $X = 11.2, Y = 0.86, Z = 3.374 \times 10^6$
(C) $X = 11.17, Y = 0.863, Z = 3.3744 \times 10^6$
(D) $X = 11.2, Y = 0.863, Z = 3.374 \times 10^6$
(E) $X = 11.17, Y = 0.8632, Z = 3.37442 \times 10^6$
2. What is the pH of a 0.050 M solution of a weak acid HA with $pK_a = 1.00 \times 10^{-3}$?
- (A) 2.17
(B) 2.30
(C) 2.70
(D) 3.00
(E) 3.30
3. When a recorded spectrum has a signal-to-noise ratio (SNR) of 3, what is the easiest method to increase the SNR by one order of magnitude, i.e., $SNR = 30$.
- (A) Decrease the noise by 10 times by using an electronic circuit.
(B) Increase the signal by 10 times by using an electronic circuit.
(C) By accumulative repetitive scans of 10 times.
(D) By accumulative repetitive scans of 30 times.
(E) By accumulative repetitive scans of 100 times.
4. The selectivity coefficient for a membrane electrode for Na^+ with respect to K^+ is reported to be 0.052. Calculate the relative error in the determination of K^+ in a solution that has a K^+ concentration of 1.00×10^{-3} M if the Na^+ concentration is 1.00×10^{-2} M. Assume that the signal for a blank was zero.
- (A) 52%
(B) 35%
(C) 26%
(D) 5.2%
(E) 2.6%

5. The following are statements about molecular luminescence spectroscopy:
- Fluorescence is independent of source intensity.
 - Fluorescence is better collected at 90° with respect to the excitation axis.
 - Linear relationship is not expected at high analyte concentration.
- (A) Statements I and II are true.
(B) Statements I and III are true.
(C) Statements II and III are true.
(D) All are true.
(E) None are true.
6. Which of the following statements does NOT represent the advantage of Raman spectroscopy over infrared (IR) absorption spectroscopy?
- (A) Raman spectroscopy is applicable to aqueous samples while IR absorption spectroscopy does not.
(B) Raman spectroscopy is more sensitive than IR absorption spectroscopy.
(C) A single Raman measurement can cover the entire range of vibrational frequencies but not in IR absorption measurement.
(D) Glass or quartz cells can be used in Raman spectroscopy but not in IR absorption spectroscopy.
(E) None of the above.
7. The distribution coefficient for iodine between CCl_4 and H_2O is 85. Calculate the concentration of I_2 remaining in the aqueous layer after extraction of 50.0 mL of 4.30×10^{-3} M I_2 with 50.0 mL of CCl_4 .
- (A) 5.12×10^{-5} M
(B) 5.06×10^{-5} M
(C) 5.00×10^{-5} M
(D) 2.50×10^{-5} M
(E) 2.56×10^{-5} M
8. Which of the following indicators is/are NOT a suitable redox indicator for the titration of $\text{Fe}(\text{CN})_6^{4-}$ with Ti^{3+} in 1 M HCl?
- Given: $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- = \text{Fe}(\text{CN})_6^{4-}$, $E^\circ = 0.356$ V; $\text{Ti}^{3+} + \text{e}^- = \text{Ti}^+$, $E^\circ = 0.77$ V (1 M HCl).
- (A) Only Indigo tetrasulfonate, $E^\circ = 0.36$ V.
(B) Only Methylene blue, $E^\circ = 0.53$ V.
(C) Only Diphenylamine, $E^\circ = 0.75$ V.
(D) Both Indigo tetrasulfonate and Diphenylamine.
(E) Both Methylene blue and Diphenylamine.

9. Which molecular process does NOT correspond to the energies of ultraviolet-visible-near infrared photons.
- I. Molecular fluorescence
 - II. Raman scattering
 - III. Nuclear magnetic resonance
 - IV. Atomic absorption
- (A) I only.
(B) II only.
(C) III only.
(D) IV only.
(E) II and III.
10. Which of the following statements about atomic spectroscopy is NOT true?
- (A) In general, atomic emission methods are better suited for multi-element analysis than atomic absorption methods.
(B) A flame atomizer is more sensitive than a nonflame atomizer.
(C) Absorption and fluorescence methods are theoretically less dependent upon temperature than emission methods.
(D) Ionization interferences are less severe in inductively coupled plasma than in flame emission spectroscopy.
(E) All of the above.
11. For a reversed-phase (non-polar stationary phase) separation, predict the order of elution of ethyl acetate, n-hexane, nitromethane, diethyl ether.
- (A) ethyl acetate, n-hexane, nitromethane, diethyl ether
(B) diethyl ether, n-hexane, ethyl acetate, nitromethane
(C) n-hexane, nitromethane, diethyl ether, ethyl acetate
(D) n-hexane, diethyl ether, ethyl acetate, nitromethane
(E) nitromethane, ethyl acetate, diethyl ether, n-hexane
12. With the same column length, the plate height of a chromatographic column can be reduced by
- (A) Increases in particle size of the packing.
(B) Increases in column diameter.
(C) Increases in thickness of the immobilized stationary phase.
(D) Increases in temperature.
(E) Increases in solvent viscosity.

13. Which of the following methods can reduce electroosmotic flow?
- (A) Lowering the pH of the running electrolyte;
 - (B) Adding ions such as $^+H_3NCH_2CH_2CH_2NH_3^+$ that adhere to the capillary wall;
 - (C) Covalently attaching silanes with neutral, hydrophilic substituents to the capillary wall.
 - (D) All of the above.
 - (E) None of the above
14. Which of the following is NOT a suitable method for separating ions with different mass-to-charge ratios.
- (A) Employing an electric field to cause an ion beam to travel in a circular path.
 - (B) Employing a magnetic field to cause an ion beam to travel in a circular path.
 - (C) Ions with same kinetic energies are passed into a field-free drift tube.
 - (D) Application of an ac electric field to ions which have been confined by a magnetic field.
 - (E) None of the above.
15. Which spectroscopic technique can give you information about the oxidation state of an element in a sample?
- (A) X-ray fluorescence
 - (B) Nuclear magnetic resonance
 - (C) Inductively coupled plasma mass spectrometry
 - (D) X-ray photoelectron spectroscopy
 - (E) Auger electron spectroscopy

II. 問答題

16. (4 分) Given the relationship $X = A + B - C$, express the absolute uncertainty x of the result X , and the corresponding relative uncertainty x/X , in terms of the absolute uncertainties a , b , and c of the observations A , B , and C , respectively.
17. (4 分) The following calibration data were obtained by an instrumental method for the determination of the species X in an aqueous solution.

<u>Concentration of X (ppm)</u>	<u>Analytical Signal</u>
0.00	0.031, 0.029, 0.034, 0.033, 0.030
2.00	0.173
6.00	0.422
10.00	0.702

A plot of analytical signal (S) versus concentration of X (C) yields $S = 0.0664C + 0.033$. What is the limit of detection (LOD) for the method?

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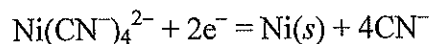
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18. (4 分) A portable photometer with a linear response to radiation registered $50 \mu\text{A}$ with a blank solution in the light path. Replacement of the blank with a standard solution (10^{-4} M) yielded a response of $20 \mu\text{A}$. On the other hand, replacement of the standard with an unknown sample yielded a response of $30 \mu\text{A}$. Calculate the concentration of the unknown solution.

19. (8 分) Compute E° for the process:

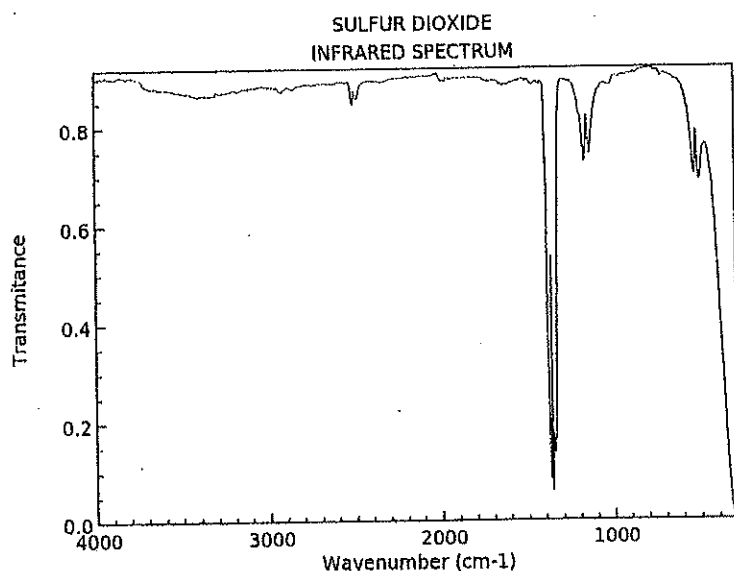


Given: formation constant for the complex is 1.0×10^{22} ; $\text{Ni}^{2+} + 2e^- = \text{Ni}(s)$, $E^\circ = -0.250 \text{ V}$.

物理化學 總分 50 分

Physical constants: $h = 6.626 \times 10^{-34} \text{ J s}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

20. Write the expression for a linear momentum operator \hat{p}_x in quantum chemistry. (3)
21. Is the wavefunction $\psi(x) = \sqrt{2/L} \sin(\pi x/L)$, $0 \leq x \leq L$, an eigenfunction of one-dimension linear momentum operator \hat{p}_x ? Please reason your answer. (4)
22. For $2p^2$ electron configuration, please write all the spin triplet-state wavefunctions. (6)
23. Below is the IR spectrum of SO_2 gas. According to the normal mode calculation, SO_2 have three vibrational normal modes with fundamental frequencies of 518, 1151, 1362 cm^{-1} , respectively. (a) Name the vibrational motion for each normal mode and assign their frequencies. (b) Why is each band in the IR spectrum split into two? (c) What is the source of band around 2500 cm^{-1} ? What cause the appearance of this band? (d) Why does the band around 1360 cm^{-1} have strongest intensity? (15)

NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

24. Thermodynamic fundamental equation for Gibbs free energy of a pure substance is given by $dG = Vdp - SdT$. (a) What is the trend of Gibbs free energy change with increase of temperature at constant pressure? This is, does Gibbs free energy increase or decrease with the increase of the temperature and by what rate? (b) What is the trend of Gibbs free energy change with increase of pressure at constant temperature? (6)
25. The equilibrium constant K of a gas phase reaction is related to the standard reaction Gibbs free energy by $\ln K = -\Delta_r G^\circ / RT$. (a) How does K change with pressure? (b) How does K change with temperature? (8)
26. The rate constant of a reaction running at 80°C increases ten times after adding a catalyst. How much the activation energy is reduced by the catalyst? (4)
27. The C-C bond energy is about 350 kJ/mole. Estimate the longest wavelength (in nm) of light that can break C-C bonds. (4)