# 國立中正大學

# 108 學年度碩士班招生考試

# 試 題

## [第2節]

系所組別	化學暨生物化學系
科目名稱	物理分析化學

#### -作答注意事項-

- ※作答前請先核對「試題」、「試卷」與「准考證」之<u>系所組別、科目名稱</u>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。

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科目名稱:物理分析化學

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系所組別:化學暨生物化學系

物理化學部分 總分50%	)分
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#### 第一部份 選擇題(單選;每題3分,共18分)

- 1. Which of the following is true regarding noncompetitive inhibitors?
  - I. They do not form covalent bonds with the active site
  - II. They alter both  $K_{\rm m}$  and  $v_{\rm max}$
  - III. They alter the shape of the active site
  - (a) I and III
- (b) II and III
- (c) III only
- (d) I only
- 2. The rate law for the reaction:  $2A + 2B \rightarrow 3C + D$  was found to be  $v = k[A]^2[B]^2$ . What is the unit of k?
  - (a)  $M^3 s^{-1}$
- (b)  $L^3 \text{ mol}^{-3} \text{ s}^{-1}$ 
  - (c)  $L^4 \text{ mol}^{-4} \text{ s}^{-1}$
- (d) L<sup>-1</sup> mol<sup>1</sup> s<sup>-1</sup>
- 3. The combustion of methanol takes place according to the reaction

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l).$$

Calculate  $\Delta H$  for the combustion of 1 mol of methanol under standard conditions. Use the following standard enthalpies of formation:

$$\Delta H^{\circ}_{f}$$
 for  $CH_{3}OH(1) = -238.5$  kJ/mol

$$\Delta H_{f}^{\circ}$$
 for  $CO_{2}(g) = -393.5$  kJ/mol

$$\Delta H^{\circ}_{f}$$
 for  $H_{2}O(1) = -285.6$  kJ/mol

(c) 
$$-1452.4$$
 kJ/mol

4. A mixture of hydrogen and chlorine remains unreacted until it is exposed to ultraviolet light from a burning magnesium strip. Then the following reaction occurs very rapidly.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

$$\Delta G = -45.54 \text{ kJ}; \Delta H = -44.12 \text{ kJ}; \Delta S = -4.76 \text{ J/K}$$

Select the statement below that best explains this behavior.

- (a) The reactants are thermodynamically more stable than the products.
- (b) The reaction has a small equilibrium constant.
- (c) The ultraviolet light raises the temperature of the system and makes the reaction more favorable.
- (d) The reaction is spontaneous, but the reactants are kinetically stable.
- 5. Consider the freezing of liquid water at  $-10^{\circ}$ C. For this process what are the signs for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ , respectively?
  - (a) + -
  - (b) + -
  - (c) - -
  - (d) + 0
- 6. As the vibrational quantum number increases, the energy separation between neighboring vibrational energy levels of a diatomic molecule
  - (a) increases
  - (b) stays the same
  - (c) decreases
  - (d) increases first and then decreases

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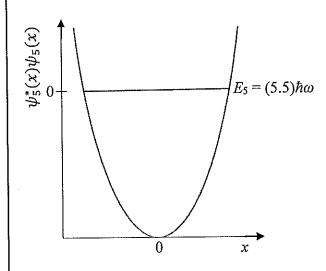
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### 第二部份 問答題 (題分示於各題題號後,共32分)

7. (10 pts) Sketch  $\psi_5^*(x)\psi_5(x)$  vs. x, where  $\psi_5(x)$  is the v=5 wavefunction of a harmonic oscillator. Describe each of the essential qualitative features of this sketch.



8. (10 pts) Spectrum of a Particle in a 1D Box: The absorption spectrum of a conjugated molecule of length L can be approximated as an electron trapped in a 1D box of the same length. Thus, the electron feels a potential

$$V(x) = \begin{cases} 0 & \text{if } 0 \le x \le L \\ \infty & \text{otherwise} \end{cases}$$

In this problem, we will use this model to make a simple picture of the electronic absorption spectrum of a conjugated molecule.

- (a) What are the energy levels available to the electron in this "molecule"?
- (b) How does the wavelength of the lowest energy absorption feature compare to the length of the molecule? Does this make sense?
- 9. (12 pts) For the photochemical H<sub>2</sub> + Br<sub>2</sub> Reaction, its mechanism is known as

$$h\nu + Br_2 \rightarrow 2Br$$
  $(k_1)$ 

$$Br + H_2 \rightarrow HBr + H$$
 (k<sub>2</sub>)

$$H + Br_2 \rightarrow HBr + Br$$
 (k<sub>3</sub>)

$$H + HBr \rightarrow H_2 + Br$$
 (k4)

$$Br + Br \rightarrow Br_2$$
  $(k_{-1})$ 

 $I_a$  is the intensity of light absorbed. Please prove that its rate law is of the following expression:

$$\upsilon_{\rm HBr} = \frac{2k_2 (1/k_{-1})^{1/2} [{\rm H_2}] [{\rm Br_2}] I_a^{1/2}}{[{\rm Br_2}] + (k_4/k_3) [{\rm HBr}]}$$

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分析化學〔每題 10 分;共五題〕

1. Briefly answer the following questions about liquid chromatography – mass spectrometry (LC-MS)

- A. Why normal phase LC is not suitable to use in LC-MS system?
- B. What kind of interference problem will arise when ion exchange LC is used?
- 2. The p-values of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) dissociation constants are pK<sub>1</sub> 6.5 and pK<sub>2</sub> 10.5, respectively.

  Please calculate the pH values of the following mixture solutions of carbonic acid and NaOH. (Only two significant figures are required; 兩位有效數字即可)
- A. The mixing volume ratio of carbonic acid and NaOH of the same concentration is 2:1.
- B. The mixing volume ratio of carbonic acid and NaOH of the same concentration is 1:1.
- 3. To extract phenol in aqueous solution using ethyl acetate solvent, what kind of carbonate buffer is suitable to use, carbonic acid/sodium bicarbonate buffer or sodium bicarbonate/sodium carbonate buffer? [Hint: the pKa of phenol is 10; the dissociation constants of H<sub>2</sub>CO<sub>3</sub> have been given in Q2.]
- 4. When the UV-VIS absorbance values of solution A and solution B are 0.3 and 0.6, respectively, in one cell of 1-cm light path, calculate the absorbance values of the following mixture solutions
- A. The mixing volume ratio of A and B is 1:1 (equal volume).
- B. The mixing volume ratio of A and B is 2:1 in one cell of which the light path is 2 cm. [Solution A and solution B are assumed NOT to interact with each other.]
- 5. The average value and standard deviation value of four measured replicates of the same sample is 4.0 g and 1.0 g, respectively.
- A. Under 95% confidence level, when the confidence interval of the above measured value is from 4.0 I to 4.0 + I, please specify the value I. (Only two significant figures are required; 兩位有效數字即可)
- B. What is the Student's t-value used to specify I?

[Hint: the Student's t-values under 95% confidence level are 3.182, 2.776, and 2.571, when the degrees of freedom of the average value are 3, 4, and 5, respectively]