

# 國立臺灣師範大學 113 學年度碩士班招生考試試題

科目：物理化學

適用系所：化學系

注意：1.本試題共 5 頁，請依序在答案卷上作答，並標明題號，不必抄題。2.答案必須寫在指定作答區內，否則依規定扣分。

## Quantum mechanics (35 points)

1. In classical and quantum mechanics, the average energies ( $E_{c.m.}$  and  $E_{q.m.}$ , respectively) can be written as

$$E_{c.m.} = \frac{\int p(E) \times E dE}{\int p(E) dE} = kT \quad \text{and} \quad E_{q.m.} = \frac{\sum p(E) \times E}{\sum p(E)} = \frac{h\nu}{\left(e^{\frac{h\nu}{kT}} - 1\right)}$$

Accordingly, we can get the energy distributions in classical and quantum mechanics ( $\rho_{c.m.}$  and  $\rho_{q.m.}$ , respectively) as

$$\rho_{c.m.} = \frac{8\pi kT}{\lambda^4} \quad \text{and} \quad \rho_{q.m.} = \frac{8\pi hc}{\lambda^5} \frac{1}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)}$$

- (A) According to the equations of  $E_{c.m.}$  and  $E_{q.m.}$ , describe the fundamental assumptions of these energy in classical and quantum mechanics. (3 points)
- (B) Set  $\rho_{c.m.}$  as y axis and  $\lambda$  as x axis, plot the energy distribution in classical mechanics. (2 points)
- (C) Set  $\rho_{q.m.}$  as y axis and  $\lambda$  as x axis, plot the energy distribution in quantum mechanics. (2 points)
2. In quantum mechanics, the kinetic energy operator for a system with mass  $m$  is

$$\hat{T} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

- (A) Write down the Schrodinger equation for a particle (with mass  $m$ ) in a one-dimensional box. (2 points)
- (B) Plot the wavefunctions for quantum number  $n = 1$  and  $2$ . (2 points)
- (C) Plot the wavefunction for quantum number  $n \rightarrow \infty$  and explain the wavefunction approaches to the motion in classical mechanics. (2 points)

# 國立臺灣師範大學 113 學年度碩士班招生考試試題

## 3. Hydrogen atom

In quantum mechanics, the Schrodinger equation for hydrogen atom is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{2Z}{r} \psi + 2E\psi = 0$$

(A) Which terms are kinetic energy and which are potential energies? (2 points)

(B) The wavefunction can be separated into radial and angular parts  $\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) = RY$ , Schrodinger equation can be separated into angular ( $Y$ ) and radial ( $R$ ) equations. The  $Y$  equation is

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] + l(l+1)Y = 0$$

Accordingly, the  $R$  equation can be expressed as

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + [A]R = 0$$

What is function  $A$  (3 points)

(C) What are quantum number and eigenvalue can we get by solving the above  $R$  equation? (4 points)

(D) Set  $\alpha^2 = -2E$ ;  $\lambda = \frac{Z}{a}$ ;  $\rho = 2\alpha r$ ,  $R$  equation can be rearranged as

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[ \frac{-l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4} \right] R = 0$$

Comparing with the associated Laguerre equation in below, find the energy  $E$  in terms of  $Z$  and  $n$  (2 points)

$$f'' + \frac{2}{x} f' + \left[ \frac{n}{x} - \frac{l(l+1)}{x^2} - \frac{1}{4} \right] f = 0$$

(E) The angular wavefunction in (B) can be further separated as  $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi) = \Theta\Phi$  and the angular equation can be separated into  $\Phi$  and  $\Theta$  equations. Knowing that  $\Phi$  equation is

$$\frac{d^2 \Phi}{d\varphi^2} + m^2 \Phi = 0$$

Accordingly, the  $\Theta$  equation can be expressed as

# 國立臺灣師範大學 113 學年度碩士班招生考試試題

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial\Theta}{\partial\theta} \right) + [B]\Theta = 0$$

What is function  $B$  (2 points)

(F) What are quantum number and eigenvalue can we get by solving the above  $\Theta$  equation? (4 points)

4. Orbital angular moment ( $L$ ), spin angular moment ( $S$ ) and total angular moment ( $J$ ) are the three important angular moments applied to identify the spectra of multi-electron atoms. The related term symbol can be represented as  $^{2S+1}L_J$ 
  - (A) For the term symbol of  $^1D_2$ , what are the values of  $S$ ,  $L$  and  $J$ ? (3 points)
  - (B) What are the two term symbols for ground-state  $Al$ , whose electron configuration is  $1s^2 2s^2 2p^6 3s^2 3p^1$ ? (2 points)

## Thermodynamics (35 points)

[Notations  $H$ : enthalpy,  $U$ : internal energy,  $S$ : entropy,  $S_{sur}$ : entropy of surroundings,  $S_{total}=S+S_{sur}$ ,  $A$ : Helmholtz free energy,  $G$ : Gibbs free energy,  $\mu$ : chemical potential,  $p$ : pressure,  $T$ : temperature,  $V$ : volume,  $V_m$ : molar volume,  $n$ : number of moles,  $R$ : ideal gas constant,  $q$ : heat,  $w$ : work,  $C_{V,m}$ : molar heat capacity at constant volume,  $C_{p,m}$ : molar heat capacity at constant pressure,  $rev$ : reversible,  $E^\theta$ : standard cell potential]

5. Thermodynamics (是非題. O: True; X: False. 5 分) When pressure is increased at constant temperature, Gibbs free energy decreases.
6. Thermodynamics (是非題. O: True; X: False. 5 分) Mixture: For an ideal solution, chemical potential of solvent in solution is always higher than the pure solvent.
7. Thermodynamics (單選題 5 分): 1.00 mol of a perfect gas at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in reversible way. ( the molar heat capacity:  $C_{V,m}=3R/2$ .  $R$  is the gas constant.) What is the value of entropy change of surroundings  $\Delta S_{surroundings}$  ?

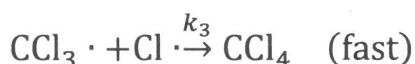
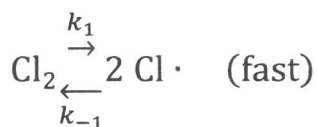
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(A)  $R \ln 3$  (B)  $300 R \ln 3$  (C)  $3 R/2$  (D)  $900 R/2$  (E)  $3 R$  (F)  $900 R$  (G)  $27 R$  (H)  $27 R e^3$  (I)  $-R \ln 3$  (J)  $-300 R \ln 3$  (K)  $-3 R/2$  (L)  $-900 R/2$  (M)  $-3 R$  (N)  $-900 R$  (O)  $-27 R$  (P)  $-27 R e^3$  (Q) 0.

8. Thermodynamics (簡答題 5 分. 無需推導。全對才給分): For an ideal gas at a temperature  $T$ , its chemical potential at pressure  $p_1$  is given by  $\mu(p_1)$ , what is its chemical potential at the pressure  $p_2$ ?
9. Thermodynamics (簡答題 5 分. 無需推導。全對才給分): Clapeyron equation is an equation describing slopes of phase boundaries. Its mathematical form is usually expressed by  $dp/dT = \Delta_{\text{transition}} X / \Delta_{\text{transition}} Y$ . What are X and Y?
10. Thermodynamics (簡答題 5 分. 無需推導): Enthalpy  $H$  is a state function and can be expressed as  $H(T, p)$ . In the case of  $(\partial H / \partial T)_p = 2$  and  $(\partial T / \partial p)_H = 1/2$ , what is the value of  $(\partial p / \partial H)_T$ ?
11. Thermodynamics/Electrochemistry (簡答題 5 分. 無需推導):  
 $\text{Cu}^{+2}_{(\text{aq})} + 2 e^- \rightarrow \text{Cu}_{(\text{s})}, \quad E^\theta = +0.3 \text{ V};$   
 $\text{Cu}^{+}_{(\text{aq})} + e^- \rightarrow \text{Cu}_{(\text{s})}, \quad E^\theta = +0.5 \text{ V}.$   
 What is the value of  $E^\theta$  (in V) of this reaction:  $\text{Cu}^{+2}_{(\text{aq})} + e^- \rightarrow \text{Cu}^{+}_{(\text{aq})}$ ?

## Kinetics (30 points)

12. What are the units of rate constant,  $k$ , in terms of molar concentration (M) and second (s) for (a) zeroth-order reaction, (b) first-order reaction, (c) second-order reaction? (6 points. For example,  $\text{M}^{-3} \cdot \text{s}^{-2}$ )
13. The proposed mechanism for the reaction  $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$  is as follows:



# 國立臺灣師範大學 113 學年度碩士班招生考試試題

Express the rate law of overall reaction,  $Rate = -\frac{d[CHCl_3]}{dt} = ?$ . (10 points)

14. A kinetic measurement of a reversible reaction,  $aA + bB \rightleftharpoons$

C ( $a$  and  $b$  are constants), is done by the stopped-flow (rapid mixing) method with monitoring the concentration of C as a function of time. The time-dependent concentration of C can be fit to the following function:

$$[C]_t = [C]_{eq}(1 - e^{-k_{obs}t})$$

and the result is given in the following table.

Trial	Volume / mL		Concentration / M		$k_{obs} / M \cdot s^{-1}$	$[C]_{eq} / M$
	A	B	A	B		
#1	0.5	0.5	$2.0 \times 10^{-3}$	$2.0 \times 10^{-5}$	$2.0 \times 10^{-7}$	$5.0 \times 10^{-6}$
#2	0.5	0.5	$2.0 \times 10^{-3}$	$1.0 \times 10^{-5}$	$2.0 \times 10^{-7}$	$2.5 \times 10^{-6}$
#3	0.5	0.5	$1.0 \times 10^{-3}$	$1.0 \times 10^{-5}$	$5.0 \times 10^{-7}$	?

Knowing that the order of the backward reaction is 1,

- Find the order of reactants A and B. (4 points)
- Find the forward and backward rate constants  $k_1$  and  $k_{-1}$ . (6 points)
- Find the equilibrium concentration of C in trial #3. (4 points)

