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 ($\boldsymbol{E_{c.m.}}$ and $\boldsymbol{E_{q.m.}}$, respectively) can be written as

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

Accordingly, we can get the energy distributions in classical and quantum mechanics ($\boldsymbol{\rho_{c.m.}}$ and $\boldsymbol{\rho_{q.m.}}$, 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 $\boldsymbol{E_{c.m.}}$ and $\boldsymbol{E_{q.m.}}$, describe the fundamental assumptions of these energy in classical and quantum mechanics. (3 points)

(B) Set $\boldsymbol{\rho_{c.m.}}$ as y axis and $\boldsymbol{\lambda}$ as x axis, plot the energy distribution in classical mechanics. (2 points)

(C) Set $\boldsymbol{\rho_{q.m.}}$ as y axis and $\boldsymbol{\lambda}$ 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 → ∞ and explain the wavefunction approaches to the motion in classical mechanics. (2 points)

3. Hydrogen atom

In quantum mechanics, the Schrodinger equation for hydrogen atom is

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

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

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

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

Accordingly, the $\boldsymbol{R}$ equation can be expressed as

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

What is function A (3 points)

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

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

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

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 $\boldsymbol{Y}(\theta,\varphi)=\boldsymbol{\Theta}(\theta)\boldsymbol{\Phi}(\varphi)=\boldsymbol{\Theta\Phi}$ and the angular equation can be separated into $\boldsymbol{\Phi}$ and $\boldsymbol{\Theta}$ equations. Knowing that $\boldsymbol{\Phi}$ equation is

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

Accordingly, the $\boldsymbol{\Theta}$ equation can be expressed as

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

What is function B (2 points)

(F) What are quantum number and eigenvalue can we get by solving the above $\boldsymbol{\Theta}$ 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 $1s^22s^22p^63s^23p^1$? (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, μ: 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^θ: 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 $\Delta S_{surroundings}$?

(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):
$Cu^{+2}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)}$, $E^\theta=+0.3$ V;
$Cu^{+}_{(aq)} + e^- \rightarrow Cu_{(s)}$, $E^\theta=+0.5$ V.
What is the value of E^θ (in V) of this reaction: $Cu^{+2}_{(aq)} + e^- \rightarrow Cu^{+}_{(aq)}$?

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, $M^{-3}\cdot s^{-2}$)

13. The proposed mechanism for the reaction $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ is as follows:

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,Cl\cdot \quad \text{(fast)}$$

$$CHCl_3 + Cl\cdot \xrightarrow{k_2} CCl_3\cdot + Cl\cdot \quad \text{(slow)}$$

$$CCl_3\cdot + Cl\cdot \xrightarrow{k_3} CCl_4 \quad \text{(fast)}$$

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

14. A kinetic measurement of a reversible reaction, $aA + bB \rightleftarrows C$ (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·s^{-1}	$[C]_{eq}$ / M
	A	B	A	B		
#1	0.5	0.5	2.0×10^{-3}	2.0×10^{-5}	2.0×10^{-7}	5.0×10^{-6}
#2	0.5	0.5	2.0×10^{-3}	1.0×10^{-5}	2.0×10^{-7}	2.5×10^{-6}
#3	0.5	0.5	1.0×10^{-3}	1.0×10^{-5}	5.0×10^{-7}	?

Knowing that the order of the backward reaction is 1,

(a) Find the order of reactants A and B. (4 points)

(b) Find the forward and backward rate constants k_1 and k_{-1}. (6 points)

(c) Find the equilibrium concentration of C in trial #3. (4 points)