國立臺灣師範大學 100 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 3 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，否則不予計分。

Quantum part:

1. From the following wavefunction information, answer the questions:

Hydrogenic radial wavefunctions $R(r)$, ($\rho = \frac{2Zr}{a_0}$)

n	ℓ	$R_{n,\ell}$
1	0	$2(\frac{Z}{a_0})^{3/2} e^{-\rho/2}$
2	0	$\frac{1}{2\sqrt{2}}(\frac{Z}{a_0})^{3/2}(2-\frac{1}{2}\rho)e^{-\rho/4}$
2	1	$\frac{1}{4\sqrt{6}}(\frac{Z}{a_0})^{3/2}\rho\, e^{-\rho/4}$
3	0	$\frac{1}{9\sqrt{3}}(\frac{Z}{a_0})^{3/2}(6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
3	1	$\frac{1}{27\sqrt{6}}(\frac{Z}{a_0})^{3/2}(4-\frac{1}{3}\rho)\rho\, e^{-\rho/6}$

The spherical harmonics $Y_{\ell,m_\ell}(\theta,\phi)$

ℓ	m_ℓ	Y_{ℓ,m_ℓ}
0	0	$(\frac{1}{4\pi})^{1/2}$
1	0	$(\frac{3}{4\pi})^{1/2}\cos\theta$
1	±1	$\mp(\frac{3}{8\pi})^{1/2}\sin\theta\, e^{\pm i\phi}$

(A) Write down the spatial part (including radial part and angular part) wave functions of $3p_x$ of He^+ atom. (The normalization factor needs not to be considered, just use N to represent it). (3 points)

(B) Locate the radial nodes (in terms of a_0) in the 2s orbital of an H atom. (2 points)

(C) What is the most probable radius (in terms of a_0) at which a 2p orbital electron will be found in the Li^{2+} atom? (5 points)

2. From the information above:

(A) What is the magnitude of the orbital angular momentum in the 3d orbital? (2 points)

(B) Give the number of radial nodes in 3d orbital. (1 point)

(C) Give the number of angular nodes in 3d orbital. (1 point)

(D) Draw the vector model to represent 3d orbital angular momentum in the space. (3 points)

3. Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (A) 3s → 1s (B) 5p → 1s (C) 5d → 3p (D) 4f → 3s (E) 5p → 4f. (5 points)

4. (A) Explain Pauli principle. (3 points)

(B) Suppose the He atom is excited to an excited state with $1s^1\,2p^1$ electron configuration then write down the lower state allowed wave function (follow Pauli principle) expression (including spatial part (Ψ_{1s}, Ψ_{2p}) and spin part (α, β)) in this configuration. (5 points)

5. The rotational moment of inertia of H_2 is I, calculate the energy of the third rotational level for the H_2 if it rotates

(A) only in a plane, (2 points), and

(B) in three dimensions (you can use $\hbar$ and I to express the answers). (3 points)

Thermodynamics part:

[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, p: pressure, T: temperature, V: volume, n: number of moles, R: ideal gas constant, q: heat, w: work, $C_{p,m}$: molar heat capacity at constant pressure, rev: reversible]

6. (單選題 10 分): The mean bond enthalpy of the C-H bond is roughly equal to which energy (in kcal/mol)? (A) 0.00001 (B) 0.0001 (C) 0.001 (D) 0.01 (E) 0.1 (F) 1 (G) 2 (H) 5 (I) 10 (J) 100 (K) 1000 (L) 10^4 (M)10^5 (N)10^6 (O)10^7(P)10^8(Q)10^9 (R) 10^{10}.

7. (單選題 5 分) In thermodynamics, for an ideal gas, $(\partial U/\partial S)_V$=
(A) H (B) U (C) A (D) G (E) p (F) –H (G) –U (H) –A (I) -G (J) RT/p (K) RT/V (L)$(RT)^2/p$ (M) $(RT)^2/V$ (N) $(pV)^2/T$ (O) $(PV)^2/R$ (P) T (Q) V (R) n (S) R .

8. (單選題 5 分.): A sample of 1.00 mol perfect gas molecules with $C_{p,m}$ = 7R/2 is put through the following cycle: (a) Constant volume heating to twice its initial temperature (the initial temperature is denoted by T), (b) Reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. What is ΔU for the step (a)?
(A) 0 (B) R ln 2 (C) R ln 3 (D) RT ln 2 (E) RT ln 3 (F) (3RT ln 2)/2 (G) (3RT ln 3)/2 (H) (5RT ln 2)/2 (I) (5RT ln 3)/2 (J) (7RT ln 2)/2 (K) (7RT ln 3)/2 (L) R/2 (M) R (N) 3R/2 (O) 5R/2 (P) 7R/2 (Q) RT/2 (R) RT (S) 3RT/2 (T) 5RT/2 (U) 7RT/2 .

9. (填充題 5 分 全對才給分) Write down the Maxwell relation $(\partial \mathbf{V}/\partial \mathbf{S})_p=(\partial \mathbf{X}/\partial \mathbf{Y})_S$ .What are **X** and **Y**? **X**= (9a) , **Y**= (9b)

10. (A) Distinguish between cell potential and electromotive force. (2 分)
(B) Distinguish between cell and battery (2 分)

11. Equilibrium constant can be expressed as a function for Gibbs energy.
(A) Please show that ΔG = -RT*lnK. (2 分)
(B) ΔG > 0 and ΔG <0 correspond to a non-spontaneous and spontaneous reactions, respectively. From the equation in (A), please show that K values of a non-spontaneous reaction is smaller than that of a spontaneous reaction and explain why the K values is smaller in a non-spontaneous reaction. (2 分)
(C) ΔG is a function of enthalpy and entropy: ΔG = ΔH – TΔS. What are the effects from enthalpy and entropy on the thermodynamic equilibrium. (2 分)

Dynamics part:

12. Brief describe the process of "fluorescence", "Phosphorescence", "Internal conversion" and "intersystem crossing" (8 points)

13. Distinguish between the "kinetics" and "dynamics". What's the similarity and difference between them?(4 points) (What can we obtain from each of them? What common physical or chemical properties can we get from both of them?)

14. Determine the half lives, $t_{1/2}$, in terms of initial concentration $[A]_0$ and rate constant k of
    (A) Zeroth and first order reactions. (2 points)
    (B) Show that $t_{1/2} \alpha [A]_0^{1-n}$ for a reaction in nth order. (2 points)
    (C) Describe the physical meaning of the initial concentration $[A]_0$ dependence or independence among reactions in zeroth, first and nth order. (4 points)

15. Describe the essential features of attractive and repulsive potential energy surfaces in the reaction paths and discuss the effectiveness of the collisional energies in translation and vibration. What is the energy distribution of the products in translational and vibrational energies? (10 points)