國立臺灣師範大學 108 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。

I. Quantum mechanics (35 points)

1. (a) In quantum mechanics, the moment of a wave is $\hat{p} = -i\hbar\frac{d}{dx}$

   Derive the kinetic energy of the wave is $\hat{T} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$ (5 points)

   (b) In quantum mechanics, the Schrodinger equation is $\hat{H}\psi = E\psi$ as $\hat{H} = \hat{T} + \hat{V}$.

   Write down Schrodinger equations for

   (i) particle-in-a-box in one dimensional space (**x**) as $\hat{V} = \begin{Bmatrix} \infty, x < 0, x > L \\ 0, 0 \leq x \leq L \end{Bmatrix}$.

   (3 points)

   (ii)harmonic oscillator in one dimensional space (**x**) as $\hat{V} = \frac{1}{2}kx^2$. (3 points)

   (iii) Hydrogen atom in the three dimensional space (**x, y, z**) as $\hat{V} = \frac{-e^2}{4\pi\varepsilon r}$

   (3 points)

2. The Schrodinger equation for Hydrogen atom in the three dimensional space (**r, θ, φ**) can be rearranged as

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

   (a) The corresponded wavefunction can be separated into radial and angular parts as

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)\psi = RY$$

   Show the Schrodinger can be rearranged in the radial and angular parts as (3 points)

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + 2Zr + 2Er^2\right] + \frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = 0$$

   (b) Knowing that the Schrodinger equation in the angular part equals to *-l(l+1)*, that is

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

What is the physical meaning of l? l corresponds to what property of the orbital? (3 points)

(c) The wavefunction in the angular part can be further separated into the two variable as

$$\boldsymbol{Y}(\theta,\varphi)=\boldsymbol{\Theta}(\theta)\boldsymbol{\Phi}(\varphi)\ or\ \boldsymbol{Y}=\boldsymbol{\Theta\Phi}$$

Show the Schrodinger equation in the angular part can be further rearranged as (3 points)

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

(d) Knowing that the Schrodinger equation for $\boldsymbol{\Phi}(\varphi)$ equals to $-m^2$, that is

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

What is the physical meaning of m? m corresponds to what property of the orbital? (3 points)

(e) Substituting $-l(l+1)$, the Schrodinger equation in the radial part becomes

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

Set $\alpha^2=-2E;\ \lambda=\frac{Z}{\alpha};\ \rho=2\alpha r$, show that the Schrodinger equation in the radial part can be rearranged as the form of associated Laguerre equation. (3 points)

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

(f) Solving the above radial equation by power series method can get the recurrence relation as

$$b_{j+1}=\frac{[2C+2Cl+2Cj-2/a]}{j(j+1)+2(l+1)(j+2)}b_j\quad as\quad C=\left(\frac{-2E}{ae^2}\right)^{1/2}\quad and\ a=\frac{\hbar^2}{me^2}$$

Show that the energy $E=-\frac{1}{n^2}\left(\frac{e^2}{2a}\right)=-\frac{me^4}{2n^2\hbar^2}$ (3 points)

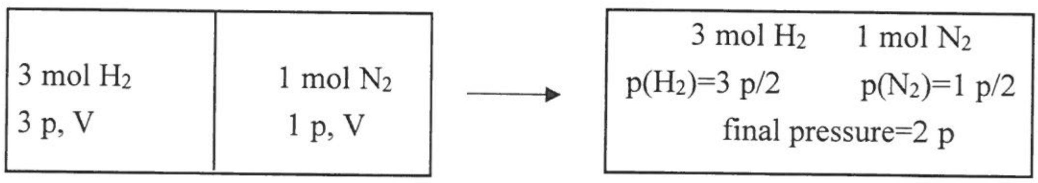
(g) From (f), What is the physical meaning of n? n corresponds to what property of the orbital? (3 points)

II. Thermodynamics (30 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, 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**]**

1. Thermodynamics(單選題 5 分): A sample of 1.00 mol perfect gas molecules with Cp,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

2. Thermodynamics: (單選題 5 分,Choose the best answer) Calculate $\Delta_{mix}G$ for mixing of the below process at a fixed temperature T: (Initially, the volume of each gas is V. Both gases are assumed ideal gas. p is pressure.)



(A) -RT ln 2 (B) -2RT ln 2 (C) -3RT ln 2 (D) -4RT ln 2 (E) -5RT ln 2 (F) -6RT ln 2 (G) RT ln 2 (H) 2RT ln 2 (I) 3RT ln 2 (J) 4RT ln 2 (K) 5RT ln 2 (L) 6RT ln 2 (M)3RT ln 3+RT ln 2 (N) –3RT ln 3 - RT ln 2 (O) 3RT ln 3+2RT ln 2 (P) –3RT ln 3 -2 RT ln 2 (Q)RT ln 3+RT ln 2 (R) -RT ln 3 - RT ln 2 (S) RT ln 3+2RT ln 2 (T) -RT ln 3 -2 RT ln 2

3. Thermodynamics (單選題 5 分): Temperature dependence of equilibrium constant of a reaction is found to fit the expression $\ln K=A+B/T+C/T^3$, what is standard reaction enthalpy? (R is ideal gas constant)

(A) RB (B) –RB (C) ATR (D) -ATR
(E) $R(B+3C/T^2)$ (F) $-R(B+3C/T^2)$ (G) $R(-AT+2C/T^2)$ (H) $-R(-AT+2C/T^2)$
(I) $R(3C/T^2)$ (J) $-R(3C/T^2)$ (K) $R(2C/T^2)$ (L) $-R(2C/T^2)$
(M) 0 (N) nART (O) –nART (P) nRT (Q) –nRT

4. Thermodynamics (簡答題 5 分，全對才給分): The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G = -a+b\ T$. a and b are constants. Calculate the value of ΔS for the process.

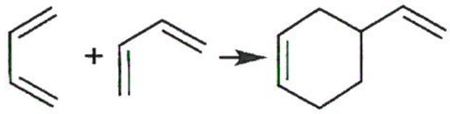
5. Thermodynamics/phase rule (簡答題 5 分，全對才給分): What is the maximum number of phases that can be in mutual equilibrium in a five-component system?

6. Thermodynamics(簡答題 5 分，全對才給分): $(\partial p/\partial T)_V=(\partial X/\partial Y)_T$ is one of Maxwell relations. What are X and Y?

III. Kinetics (35 points)

1. Kinetic measurement of a specific first-order reaction was done at various temperatures. At 300K, the rate constant was $1.000\times10^{-4}\ s^{-1}$; at 450K the rate constant was $2.718\times10^{-4}\ s^{-1}$.
   (a) Find the activation energy of this reaction. (6 points)
   (b) Predict the rate constant at 360K. (4 points)

2. Butadiene, C_4H_6, dimerizes in a Diels-Alder condensation reaction to yield a substituted cyclohexane, C_8H_{12}:



$$2C_4H_6(g) \rightarrow C_8H_{12}(g)$$

Given the data obtained from a gas-phase experiment in a fixed container at a constant temperature. The initial partial pressure of C_4H_6 and C_8H_{12} are 5000 and 0 torr, respectively. Assume ideal gas behavior for both molecules.

Time (s)	Total pressure (torr)
0	5000
500	3750
1500	3125
3500	2812.5

(a) Make a linear plot to show this condensation reaction is a second-order reaction. (8 points)

(b) Find the rate constant, k. (5 points, Using the following rate law.)

$$-\frac{1}{2}\frac{dP_{C_4H_6}}{dt} = \frac{dP_{C_8H_{12}}}{dt} = kP_{C_4H_6}^2$$

3. The result of a kinetic experiment is summarized in the following table.

$[A]_0$	$[B]_0$	Half-life of A (s)
0.001M	1.0M	100s
0.002M	1.0M	100s
0.001M	0.5M	400s
0.002M	0.25M	?

The rate law can be written as

$$-\frac{d[A]}{dt} = k[A]^m[B]^n$$

(a) Find the order of the reactant A and B (m and n). (6 points)

(b) Find the rate constant, k. (4 points)

(c) Predict the half-life of A when $[A]_0$=0.02M and $[B]_0$=0.25M. (2 points)