

國立臺灣師範大學 107 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. The moment for a particle in classical mechanics is $p = mV$ and in quantum mechanics is $\hat{p} = -i\hbar \frac{d}{dx}$

(a) What is the difference of moment between classical and quantum mechanics? (3 points)

(b) The kinetic energy is $p^2/2m$, what are the kinetic energies in classical and quantum mechanics. (3 points)

2. Write down the Schrodinger equations for (9 points)

(a) particle-in-a-box in two dimension as the related potential \hat{V} is

$$\left\{ \begin{array}{l} \hat{V} = \infty: x < 0, x > a; y < 0, y > b \\ \hat{V} = 0: 0 \leq x \leq a; 0 \leq y \leq b \end{array} \right\}$$

(b) harmonic oscillator in one dimension as the related potential $\hat{V} = \frac{1}{2}kx^2$

(c) hydrogen atom in three dimension as the related potential energy $\hat{V} = \frac{-e^2}{4\pi\epsilon r}$

3. Solve the Schrodinger equations in Question 2(a)

(a) Separate the Hamiltonian and wavefunctions in x and y coordinates, as

$\hat{H} = \hat{H}_x + \hat{H}_y$ and $\psi(x,y) = X(x)Y(y)$. Show the Schrodinger equation can be separated as $\hat{H}_x X(x) = E_x X(x)$ and $\hat{H}_y Y(y) = E_y Y(y)$ in x and y coordinates, respectively. (3 points)

(b) Solve the Schrodinger and find the energy of E_x and E_y (3 points)

4. Solve the Schrodinger equation in Question 2(b)

The solution for the Schrodinger equation in Question 2(b) is $\varphi = e^{-\frac{\alpha x^2}{2}} H_n(x)$ as $H_n(x)$ is Hermite polynomial. The recurrence relation for the coefficients (a_n) of Hermite polynomial is

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$$a_{n+2} = \frac{\alpha + 2n\alpha - \frac{2mE}{\hbar^2}}{(n+1)(n+2)} a_n \text{ as } \alpha = \frac{\sqrt{k m}}{\hbar}$$

Show the energy is

$$E = \left(n + \frac{1}{2}\right) \hbar \omega, \text{ where } \omega = \sqrt{\frac{k}{m}} \quad (3 \text{ points})$$

5. Solve the Schrodinger equation in Question 2(c)

(a) The angular part of the Schrodinger equation in Question 2(c) is

$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y(\theta, \varphi)}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2} = -cY(\theta, \varphi)$, as $Y(\theta, \varphi)$ is associated Legendre polynomial and c is square of angular momentum. The recurrence relation for the coefficients (a_j) of associated Legendre polynomial

$$a_{j+2} = \frac{[(j + |m|)(j + |m| + 1) - \frac{c}{\hbar^2}]}{(j + 1)(j + 2)} a_j$$

Show the angular momentum is

$$c = l(l + 1)\hbar^2, \text{ where } l = (j + |m|) \quad (3 \text{ points})$$

(b) The radial part of the Schrodinger equation in Question 2(c) is

$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \left(-\frac{l(l+1)}{r^2} + \frac{2Z}{r} + 2E \right) R(r) = 0$ as $R(r)$ is associated Laguerre functions and E is energy. The recurrence relation for the coefficient (b_j) of associated Laguerre polynomials

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

show the energy as

$$E = -\frac{Z^2}{n^2} \left(\frac{e^2}{2a}\right) = -\frac{Z^2 m e^4}{n^2 \hbar^2}, \text{ where } n = (j + l + 1) \quad (3 \text{ points})$$

6. The wavefunction of $1s^2$ can be written the Slater determinant

$$\varphi(1,2) = \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 1s(1)\beta(1) & 1s(2)\beta(2) \end{vmatrix}$$

(a) Write down the wavefunction of $1s^2$ and show that the wavefunction is antisymmetric $\varphi(1,2) = -\varphi(2,1)$ (3 points)

(b) Write down the Slater determinant for the wavefunction of $1s^1 2s^1$. (2 points)

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II. Thermodynamics (30 points)

[Notations H: enthalpy, U: internal energy, S: entropy, S_{sur} : entropy of surroundings, $S_{\text{total}}=S+S_{\text{sur}}$, 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) Consider an adiabatic reversible process of a monoatomic ideal gas of 1 mole. The initial state is (V_1, T) , where V and T are volume and temperature, respectively. The volume of the final state is V_2 . The entropy change, ΔS , of this process is:
(A) R (B) $R \ln (V_2/V_1)$ (C) $R [(V_1/V_2)^{2/3}-1]$ (D) $RT [(V_1/V_2)^{3/2}-1]$
(E) $2R$ (F) $2R \ln (V_2/V_1)$ (G) $2R [(V_1/V_2)^{2/3}-1]$ (H) $2RT [(V_1/V_2)^{3/2}-1]$
(I) $3R$ (J) $3R \ln (V_2/V_1)$ (K) $3R [(V_1/V_2)^{2/3}-1]$ (L) $3RT [(V_1/V_2)^{3/2}-1]$
(M) $3R/2$ (N) $3R \ln (V_2/V_1)/2$ (O) $3R [(V_1/V_2)^{2/3}-1]/2$ (P) $3RT [(V_1/V_2)^{3/2}-1]/2$
(Q) $5R/2$ (R) $5R \ln (V_2/V_1)/2$ (S) $5R [(V_1/V_2)^{2/3}-1]/2$ (T) $5RT [(V_1/V_2)^{3/2}-1]/2$
(U) $7R/2$ (V) $7R \ln (V_2/V_1)/2$ (W) $7R [(V_1/V_2)^{2/3}-1]/2$ (X) $7RT [(V_1/V_2)^{3/2}-1]/2$
(Y) 0 (Z) none of the above.
2. Thermodynamics (單選題 5 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} .
3. Thermodynamics: (單選題 5 分, Choose the best answer) Which equation determines the boundary of phase transition, (choose the best answer)
(A) Clausius equation (B) Clapeyron equation (C) Schrodinger equation
(D) Boltzmann equation (E) Poisson equation (F) Huckel equation.
(G) Nernst equation (H) van Hoff equation (I) van der Waals equation
(J) Hemholtz equation (K) Planck equation.
4. Thermodynamics (單選題 5 分. Choose the best answer.) In thermodynamics, ΔH (H denotes enthalpy) represents:

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- (A). maximum work at constant temperature (T).
- (B). maximum work at constant pressure (p).
- (C). maximum work at constant volume (V).
- (D). heat at constant T, no additional (non-expansion) work.
- (E). heat at constant p, no additional (non-expansion) work.
- (F). heat at constant V, no additional (non-expansion) work.
- (G). work at constant T and V.
- (H). work at constant T and p.
- (I). work at constant V and p.
- (J). heat at constant T and V.
- (K). heat at constant T and p.
- (L). heat at constant V and p.
- (M). heat at constant T and V, no additional work.
- (N). heat at constant T and p, no additional work.
- (O). heat at constant V and p, no additional work.
- (P). maximum additional (non-expansion) work at constant T and V.
- (Q). maximum additional (non-expansion) work at constant T and p.
- (R). maximum additional (non-expansion) work at constant V and p.
- (S). heat at constant T.
- (T). heat at constant p.
- (U). heat at constant V.
- (V). work at constant T and V, no additional work.
- (W). work at constant T and p, no additional work.
- (X). work at constant V and p, no additional work.

5. 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) $R(3C/T^2)$ (F) $-R(3C/T^2)$
- (G) $R(2C/T^2)$ (H) $-R(2C/T^2)$ (I) $R(B+3C/T^2)$ (J) $-R(B+3C/T^2)$
- (K) $R(-A/T + 2C/T^2)$ (L) $-R(-A/T + 2C/T^2)$ (M) 0 (N) nART (O) -nART
- (P) nRT (Q) -nRT

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

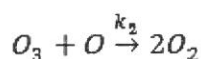
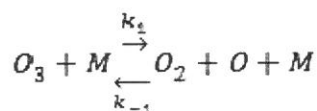
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III. Kinetics (35 points)

1. An experiment was carried out for determining the kinetics of a bimolecular irreversible reaction, $A + B \xrightarrow{k} P$. Use the results in the following table:

Temperature	Initial concentration of B	time	Concentration of A
300K	0.1M	0	$1.00 \times 10^{-4} \text{M}$
		69.3s	$5.00 \times 10^{-5} \text{M}$
		100s	$3.68 \times 10^{-5} \text{M}$
450K	0.0369M	0	$1.00 \times 10^{-4} \text{M}$
		69.3s	$5.00 \times 10^{-5} \text{M}$
		100s	$3.68 \times 10^{-5} \text{M}$

- (a) Determine the rate constant, k , at 300K and 450K. (8 points)
 (b) Determine the activation energy of the reaction. (7 points)
2. The mechanism of stratospheric ozone reaction is following:



Each step is an elementary step.

- (a) Write down the rate laws (differential form) for $[\text{O}_3]$ and $[\text{O}]$. (4 points)
 (b) Employing the steady-state approximation, show that:

$$\frac{d[\text{O}_3]}{dt} = k_{app} [\text{O}_3] [\text{M}]$$

and express the apparent rate constant, k_{app} , in terms of k_1 , k_{-1} , k_2 , and concentrations of species involved. (10 points)

- (c) What circumstance makes the depletion rate of ozone second-order to the ozone concentration? (6 points)