

國立臺灣師範大學 103 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。

Thermodynamics Part (30 分)[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 (簡答題, (a)小題:2分, (b)小題:3分): Use the following notations for the following questions: F, C, P, which are number of degree of freedom, number of components, and number of phases, respectively. (a) Write down mathematical expression of the phase rule. (b) briefly show how it is derived mathematically.
2. Thermodynamics (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) T (G) V (H) n (I) R (J) RT/p (K) RT/V (L) $(RT)^2/p$ (M) $(RT)^2/V$ (N) $(pV)^2/T$ (O) $(pV)^2/R$ (P) $-H$ (Q) $-U$ (R) $-A$ (S) $-G$.
3. Thermodynamics (單選題 5 分, choose the best answer): 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} .
4. Thermodynamics (單選題 5 分, Choose the best answer): The van't Hoff equation is $d(\ln K)/dT =$
(A) $\Delta U/(RT^2)$ (B) $\Delta(U-TS)/(RT^2)$ (C) $-\Delta U/(RT^2)$ (D) $-\Delta(U-TS)/(RT^2)$
(E) $\Delta H/(RT^2)$ (F) $\Delta(H-TS)/(RT^2)$ (G) $-\Delta H/(RT^2)$ (H) $-\Delta(H-TS)/(RT^2)$
(I) $\Delta A/(RT^2)$ (J) $\Delta(A-TS)/(RT^2)$ (K) $-\Delta A/(RT^2)$ (L) $-\Delta(A-TS)/(RT^2)$
(M) $\Delta G/(RT^2)$ (N) $\Delta(G-TS)/(RT^2)$ (O) $-\Delta G/(RT^2)$ (P) $-\Delta(G-TS)/(RT^2)$.
5. Thermodynamics (單選題 5 分, choose the best answer): Clapeyron equation is an equation describing slopes of phase boundaries. Its mathematical form is usually expressed as $dp/dT = \Delta_{transition} X/\Delta_{transition} Y$ where X and Y are thermodynamical quantities which are needed to be identified. (X, Y)= (A) (p,S) (B) (p,V) (C) (p,T) (D)(S,V) (E) (S,T) (F) (S,p) (G) (V,S) (H) (V,T) (I) (V,p) (J) (T,S) (K) (T,V) (L) (T,p).
6. Thermodynamics (填充題 5 分 全對才給分): Write down the fundamental equation, which is combination of the 1st and 2nd laws. $dU = \underline{(6)}$

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Quantum part (35 分)

7. A particle with mass m is in a state described by the wavefunction

$$\psi(x) = ne^{ikx} + me^{-ikx}, \text{ where } n^2 + m^2 = 1, \text{ answer the followings:}$$

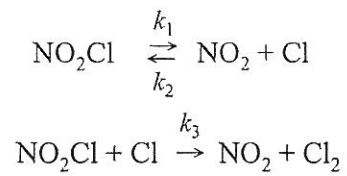
- (a) If we try to measure the linear momentum of this wave function, what will be the possible values that we could obtain each time? (2 分)
- (b) If we want to be certain of 70% measurement to obtain $+\hbar k$, then what will be the values of n and m in the above wave function. (2 分)
- (c) What is the kinetic energy of the particle if $n = m = 1$? (2 分)
8. (a) Give the ground-state electron configurations of H_2O (total 10 electrons, if the molecular orbital energy order is $1a_1 < 2a_1 < 1b_2 < 3a_1 < 1b_1 < 4a_1$) (3 分)
- (b) According to the above electron configuration, what is the ground molecular term symbol for H_2O ? (3 分)
9. (a) Which of the following molecules may show a pure rotational microwave absorption spectrum: (A) H_2 (B) H_2O (C) HCl (D) CO_2 (E) CH_4 (F) NO (4 分)
- (b) Which of the following molecules may show a pure rotational Raman spectrum: (A) CH_2Cl_2 (B) H_2 (C) CH_4 (D) SF_6 (E) CO_2 (F) CO (3 分)
10. For the linear molecule of LiH_2 , for all the vibration modes (give the name such as symmetric stretch, or asymmetric stretch or bending) which may show infrared active or Raman Active? (6 分)
11. Briefly explain or answer the followings: (a) ortho hydrogen (2 分) (b) para hydrogen (2 分) (c) Franck-Condon principle (2 分) (d) Fluorescence and (2 分) (e) phosphorescence (2 分)

Kinetics Part (35 分)

12. Dinitrogen pentoxide, N_2O_5 , decomposes with a rate constant $k = 0.15 \text{ s}^{-1}$ at 353 K ($\text{N}_2\text{O}_5 \rightarrow$ products). (a) What is the half-life for the decomposition of N_2O_5 at 353 K? (5 分) (b) If the initial concentration of N_2O_5 is 0.0567 M, what will be the concentration of N_2O_5 after 2.0 seconds? (5 分) (c) How much time will be needed as the concentration of N_2O_5 decreases from 0.0567 M to 0.0135 M? (5 分)
13. A gas composed of molecules takes part in a chemical reaction at 1.0 atm with another gas consisting of molecules of about the same size and mass to form a gas-phase product. The activation energy for the reaction is 25 kJ/mol. Use the collision theory to calculate the ratio of the reaction rate constant at 320 K relative to that at 300 K. (10 分)

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14. The compound NO_2Cl is thought to undergo the reaction of decomposition via the following mechanism:



- (a) What is the reaction equation for the decomposition of NO_2Cl ? (5 分)
(b) Derive the rate law for the production of Cl_2 using the steady-state approximation. (5 分)

