

說明：1. 請依序作答並標明題號。

2. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

1. The reaction $A + B \rightarrow C$ takes place in two steps by the mechanism
 $2 A \rightleftharpoons D$ followed by $B + D \rightarrow A + C$ with rate constant k_2 . The first step comes to a rapid equilibrium with equilibrium constant K_1 . Derive an expression for the rate of formation of C in terms of K_1 , k_2 , $[A]$, and $[B]$. (6%)
2. It is often said that near room temperature, a chemical reaction rate doubles with every 10° rise in temperature. Calculate the activation energy of a reaction at 300°K that obeys this rule exactly. (6%)
3. Please explain the following photophysical processes in a photochemical reaction.
 - a. resonance fluorescence (2%)
 - b. intersystem crossing (ISC) (2%)
 - c. internal conversion (IC) (2%)
4. It is known that entropy changed is greater than zero ($dS > 0$) for a spontaneous reaction. Based on this, please show that dG (Gibbs free energy) < 0 is required for a spontaneous reaction. (8%)
5. An ideal gas absorbs 9410 J of heat when it is expanded isothermally (at 25°C) and reversibly from 1.5 dm^3 to 10 dm^3 . How many moles of the gas are present? (6%)
6. The constant-pressure heat capacities of gaseous hydrogen, oxygen, and water are 29.0, 29.5, and $33.6 \text{ J mole}^{-1} \text{ K}^{-1}$, respectively. Assume that heat capacities are independent of temperature. The enthalpy of formation of gaseous water at 25°C is $-241.82 \text{ KJ mol}^{-1}$. What is its value at 100°C ? (8%)
7. If the ionization constant of a molecule could be described by the equation
$$\ln K = 7 - 1850/T - 0.002T$$
between 5°C and 55°C . Calculate values of ΔG° and ΔH° for the ionization at 50°C . (10%)

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8. Evaluate the following commutators:
- (a) $[d/dx, x^2]$ (4%)
- (b) $[\hat{x}, \hat{p}_x]$, \hat{x} : operator corresponding to the x coordinate, \hat{p}_x : operator for the x component of linear momentum. (4%)
9. If ψ_1 , ψ_2 , and ψ_3 are wave functions with a degenerate energy E , please show that any linear combination $c_1\psi_1 + c_2\psi_2 + c_3\psi_3$ is still a wave function. (8%)
10. (a) Find the term symbols, $^{2S+1}L_J$, resulting from non-equivalent electrons, pp . (6%)
- (b) Please determine the ground-state term symbol for d^6 electronic configuration. (4%)
11. (a) Please write the complete Hamiltonian operator for hydrogen molecule (H_2). (3%)
- (b) What is Born-Oppenheimer approximation? (3%)
- (c) If Born-Oppenheimer is applied, then how to construct molecular Hamiltonian operator for H_2 . (3%)
12. Find the normalization constant for the molecular orbital $c(1S_A + 1S_B)$ in terms of the overlap integral S , where c is normalization constant. (6%)
13. (a) Could we observe pure rotational spectrum for O_2 molecule? why? (3%)
- (b) For CO_2 , please specify the vibrational mode(s) with infrared active and explain your reason. (6%)