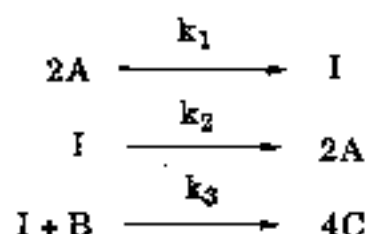


八十六學年度 化學系 系(所) 化學系 組碩士班研究生入學考試
 科目 物理化學及分析化學 科號 0603 0703 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

1. The reaction mechanism of an overall reaction $2A + B \xrightarrow{k_{\text{exp}}} 4C$ has been proposed to proceed through following elementary steps



where I is an unstable intermediate. Rate constants k_1 , k_2 and k_3 have an activation energy of E_1 , E_2 and E_3 , respectively.

- Derive the rate law for the overall reaction using the steady state approximation. (5%)
 - If the rate of the third step (R_3) is much faster than the rate of the second step (R_2), what is the kinetic order (n) and the activation energy (E_{exp}) of the overall reaction? (5%)
- Estimate the maximum heat capacity (C_V) at constant volume of a CO_2 molecule. (5%)
 - What is Clausius inequality? (5%) Try to proof it. (5%)
 - What are the wavelength and kinetic energy of the electron in a beam of electrons accelerated by a voltage increment of 100 V. You do not have to get the final numerical answer; however you do have to plug in all the constants neatly into your equations. (3%)
 - Show that the variance defined as $\sigma_f^2 = \langle (x - \langle x \rangle)^2 \rangle$ can be expressed as $\sigma_f^2 = \langle x^2 \rangle - \langle x \rangle^2$. (2%)

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6. Explain the flowing terms briefly. (20%)
 - (a) Two operators being commute.
 - (b) Well behaved state function.
 - (c) Linear operator, and Hermitian operator.
 - (d) LCAO-MO. For example the minimum basis wave function of the ground state of H_2 .
 - (e) σ bond and π bond.
 - (f) Term symbol.
 - (g) How do you determine the ground state term of NH_3 ?
 - (h) Bonding and antibonding.
 - (i) Microwave spectra.
 - (j) The selection rules of electronic transition.
7. Explain the following items (16%)
 - (a) precision of an analytical method
 - (b) coprecipitation
 - (c) peptization of colloids
 - (d) precipitate contamination by occlusion
8. Describe the principle of "background absorption corrector" used in atomic absorption spectrometer. (9%)
9. Link the kinds of substances to which each of the following kinds of chromatography is the most applicable:
 - (a) gel-filtration; (b) ion-exchange; (c) liquid-partition;
 - (d) gas-liquid; (e) gas-solid. (10%)
10. Briefly describe the following terms:
 - (a) sputtering; (b) releasing agent; (c) EPMA;
 - (d) voltammetry; (e) ICP-AES (10%)

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11. What are the advantages of a Fourier transform infrared spectrometer compared with a dispersive instrument? (5%)

Some useful constants:

$$m_e = 9.10953 \times 10^{-31} \text{ kg}, \text{amu} = 1.66056 \times 10^{-27} \text{ kg}, h = 6.62618 \times 10^{-34} \text{ J}\cdot\text{s}, e = 1.60219 \times 10^{-19} \text{ C}, a_0 = 5.29177 \times 10^{-11} \text{ m}$$