八十六學年度 化學系 系（所） 化學 應用化學 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 $2A + B \xrightarrow{k_{exp}} 4C$ has been proposed to proceed through following elementary steps

$$2A \xrightarrow{k_1} I$$

$$I \xrightarrow{k_2} 2A$$

$$I + B \xrightarrow{k_3} 4C$$

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.

(a) Derive the rate law for the overall reaction using the steady state approximation. (5%)

(b) 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%)

2. Estimate the maximum heat capacity (C_v) at constant volume of a CO_2 molecule. (5%)

3. What is Clausius inequality? (5%) Try to proof it. (5%)

4. 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%)

5. Show that the variance defined as $\sigma_x^2 = ((x - \langle x \rangle)^2)$ can be expressed as $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$. (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:

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