國立成功大學

112學年度碩士班招生考試試題

編　號：44

系　所：化學系

科　目：物理化學
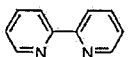
日　期：0207

節　次：第 1 節

備　註：不可使用計算機

※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

計算與問答題: (需寫出推導和計算過程否則不予計分)

1. (a) For a real gas following the $P = RT/(V_m - b) - a/V_m^2$ eqaution, please calculate the critical compression factor Z_c value of the gas. (6%)

   (b) Derive internal pressur of the real gas $\pi_T = T (\partial p/ \partial T)_v - p$ (3 %)

   (c) Please calculate π_T of the real gas. (3 %)

2. (a) If a spontaneous change occurs with a decrease in entropy of the system, why | work | $< |\Delta U|$? (4 %)

   (b) Please use the chemical reaction of　$2A + 3B \longrightarrow C + 2D$ to derive the equation of $\Delta_r G = \Delta_r G^o + RT \ln Q$. (6 %)

3. (a) What is the thermodynamic criterion for the equilibrium between phase A and phase B? (3%)

   (b) In a phase diagram (pressure vs. temperature) of a CO_2, please derive the slope of liquid-solid boundary. (4 %)

   (c) Is the slope of gas-solid boundary of a CO_2 negative, positive? Why? (3 %)

4. (a) For a regular solution of A and B, please derive the Margules equations: $\ln \gamma_A = \beta \chi_B^2$ and $\ln \gamma_B = \beta \chi_A^2$. ($\beta$ is a dimensionless parameter to measure the energy AB interactions related to that of the AA and BB interactions.) (5 %)

   (b) Based on the following result, please derive the Henry's law constant $K = p_A^* \exp\beta$ (3 %)

5. (a) Draw a wavefunction diagram to describe the tunneling effect of particle in a one-dimension box with energy barriers of V and energy wall thickness of L. (4%)

   (b) Draw a representative wavefunction of a particle in a potential decreasing toward the right (as right figure). (4 %)

6. (a) Derive the Beer-Lambert law:　$A = \varepsilon[J]l$, l: length of the cell　(4 %)

   (b) Why does the $[Co(H_2O)_6]^{2+}$ complex ion have low ε value for the d-d transition in the visible-light region? (4 %)

   (c) Why does the $[Os(bipy)_3]^{2+}$ complex ion have long-life exited state and large ε value widely used as photocatalysts. (4%)　　bipy:　
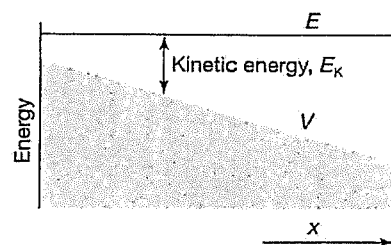
7. (a) Draw a representative figure to estimate the value of the overlap integral between $\psi 2s(A)$ and $\psi 2p_x(B)$ in the A—B molecule? (Hint: z is the molecular axis.) (3 %)

(b). Use the following Hückel approximation matrix to estimate the delocalization energy of the π molecular orbitals and draw the HOMO and LUMO shapes of the molecular orbitals in butadiene. (7 %) (Hint: The energies of tπ orbital in ethene are $\alpha + \beta$ and $\alpha - \beta$)

$$E = \begin{pmatrix} \alpha+1.62\beta & 0 & 0 & 0 \\ 0 & \alpha+0.62\beta & 0 & 0 \\ 0 & 0 & \alpha-0.62\beta & 0 \\ 0 & 0 & 0 & \alpha-1.62\beta \end{pmatrix} \quad C = \begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

8. (a) Derive the rate law of the relaxation method for determination the rate constants k and k'.

$$A \rightleftharpoons B \quad \text{(forward: k ; reverse: k')} \quad (6 \%)$$
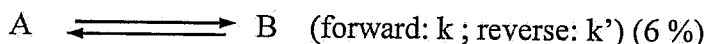
(b) Please give the phenomenological equation and define the coefficients for
(1) diffusion; (2) the flux of x-momentum in the z-direction. (4 %)

9. (a) It is well known that the Michaelis-Menten mechanism is widely used to explain the Kinetics of the enzyme reactions. Please derive an equation to prove the right-hand plot. (6 %)

(b) Please calculate the k_{cat} and catalytic efficiency (ε) of enzyme reaction at initial concentration of enzyme = $[E]_0$ (4 %)
(Hint: explain in the a, b and $[E]_0$)
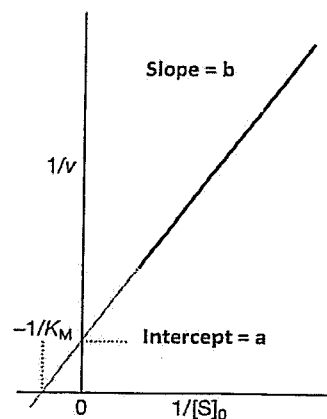
10. (a) Using the right-hand figure, to justify $\sigma(\varepsilon) = (1 - \varepsilon_a / \varepsilon) \sigma$. (5 %)

(b) Calculate $\sigma(\varepsilon) = ?$ at $\varepsilon = 0.6 \, \varepsilon_a$ (2 %)

(c) Based on the $\sigma(\varepsilon)$, please write a simple integral equation to explain the rate constant k. (3 %)