

系所組別： 化學系

考試科目： 物理化學

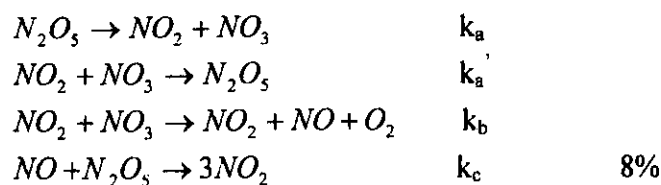
考試日期： 0307，節次： 1

※ 考生請注意：本試題 可 不可 使用計算機

Your answers must be written on the “Answer Sheet” and must be arranged in the order of the numbered questions (1-12)

$$R_{1,0}(H) = 2 \left[\frac{Z}{a_0^3} \right]^{1/2} \exp(-Zr/a_0); \quad \int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}}$$

- Show that the change of entropy (ΔS) for a perfect gas is greater than that for a van der Waals gas following the state function $p = \frac{nRT}{V-nb} - \frac{n^2}{V^2}$. 8%
- Describe the relative extents of “the variation of the Gibbs energy with the temperature of a substance” in different phases (gas, liquid and solid) by their G-T plots. 8%
- The Joule coefficient (μ_J) is defined as $\mu_J = (\partial T / \partial V)_U$. Show that this thermodynamic quantity can be related to the expansion coefficient and isothermal compressibility by $\mu_J C_V = p - \alpha T / \kappa_T$. 8%
- Calculate the vapor pressure of benzene at 293K using the data for benzene: $\Delta_{\text{vap}} H^\circ = 30.8 \text{ kJmol}^{-1}$ at the normal boiling point 353K. 6%
- Describe (a) the phase rule, (b) the level rule and (c) the eutectic mixture, respectively. 6%
- Derive the rate law for the Michaelis-mechanism of enzyme catalysis and give the Lineweaver-Burk plot of $1/v$ against $1/[S]_0$. 8%
- Derive the rate law for the decomposition of N_2O_5 generating NO_2 and O_2 based on the mechanism:



(背面仍有題目,請繼續作答)

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8. a) Show that the deBroglie ($\lambda = h/p$) can rationalize the Bohr's postulation of the quantization of the angular momentum ($mvr = n\hbar$).
- b) Show that the deBroglie's equation can be derived by solving the Schrodinger equation for the one-dimensional particle-in-a-box model. 12%
9. (a) Give the origins of the Heisenberg uncertainty principle based on the nature of matter and on the quantum mechanics (hint: operators).
- (b) How does the Heisenberg's uncertainty principle account for the spectral widths, e.g. in NMR spectroscopy? 8%
10. (a) Give the Hamiltonians for the He atom and the molecular cation H_2^+ , respectively.
- (b) Which of the Schrodinger equations, respectively, for the above two systems can not be solved exactly? And why?
- (c) Name the two approximate methods that can be employed to treat the trouble in problem 10(b). 12%
11. Evaluate the mean radius of the 1s orbital of hydrogen orbital. 8%
12. (a) How does MO theory account for the polarity of the HF molecule.
- (b) Explain, employing the MO theory, the relative ionic characters of the CH bonds in H_3CCH_3 , H_2CCH_2 and $HCCH$ molecules. 8%