國 立 清 華 大 學 命 題 紙

八十六學年度 生命科學 系（所）分生組乙、丙 生醫組乙 組碩士班研究生入學考試

科目 物理化學 科號 1004、1103 1304 共 2 頁第 1 頁 *請在試卷【答案卷】內作答

Some equations or constants that you might need in solving the following problems:

a. The eigenvalues of a harmonic oscillator are $(n+1/2)\hbar\omega$

b. $\hbar = 6.626 \times 10^{-34}\ Js$ c. 1 cal = 4.184 J

d. $\sqrt{2} = 1.414$; $\sqrt{3} = 1.732$; $\sqrt{5} = 2.236$

e. $e^{x+y} = e^x \cdot e^y, e^8 \cong 3{,}000, e^9 \cong 8{,}100, e^{10} \cong 22{,}000, e^{11} \cong 60{,}000, e^{12} \cong 160{,}000$

f. R = 8.00 J/mol K at 27°C

(1) Explain the following terms (15%)

(a) The spin-lattice relaxation time (usually denoted by T_1)

(b) The residual entropy

(c) The canonical ensemble

(d) The nuclear Overhauser effect

(e) Quantum yield

(2) Consider the one-dimensional Schrodinger equation with

$$V(x) = \begin{cases} \frac{m}{2}\omega^2 x^2 & \text{for } x > 0 \\ \infty & \text{for } x < 0 \end{cases}$$

Find the energy eigenvalues. (10%)

(3) Use the Huckle approximation to find the π-electron binding energy of both ethene and butadiene, respectively. What is the delocalization energy of butadiene? [hint: use α and β as the diagonal and off-diagonal elements, respectively] (15%)

(4) (a) Show that for a simple reaction $A \underset{k_b}{\overset{k_a}{\longleftrightarrow}} B$, the relaxation time τ is related to the rate constants by $\frac{1}{\tau} = k_a + k_b$

(b) Show that for a simple reaction $A \xrightarrow{k_1} B$, the half-life, $t_{1/2}$, does not depend on its initial concentration, $[A]_0$, but depend on its first order rate constant for the reaction, k_1. (15%)

(5) The VSEPR (valence-shell electron-pair repulsion) method provides a simple, resonably accurate means of predicting molecular sharps. According to the VSEPR method, the geometry is determined by the number of pairs of valence electrons around the central atom of the molecule. (15%)

(a) Use H_2O as an example to explain how VSEPR method work. [Hint: show its electron-dot formula, explain why its bond angle is less than 109.5 °]

(b) Predict the HCH bond angle of $H_2C{=}CH_2$.

(c) Predict the bond angles of SF_4.

(6) $\langle \varepsilon_{tr} \rangle = \frac{3}{2}kT$, $C_{V,m} = \frac{3}{2}R$, $\Delta G^\circ = -nF\varepsilon^\circ$, $\upsilon = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, $C_t = TV\alpha^2/k$

$\Delta G^\circ = -RT\ln K^\circ$, $\upsilon = (3RT/M)^{1/2}$, $U_n = \frac{3}{2}NkT$, $<N_i>/N = e^{-\varepsilon_i/kT}/Z$

$\varepsilon = \varepsilon^\circ - \frac{RT}{nF}\ln\left[\prod_i (a_i)^{\nu_i}\right] = \varepsilon^\circ - \frac{RT}{nF}\ln Q$ Which one of the above equation is suitable

to do the calculation of [hint: pick up only one equation for each calculation] (15%)

(a) the average molecular transitional energy?

(b) the root-mean-square speed of gas molecules?

(c) the heat capacity of an ideal monatomic gas?

(d) electrolyte activity coefficients from cell emf data?

(e) populations of molecular states?

(7) Many antibiotics (Ab) function by binding to double-stranded DNA. The thermodynamics of binding of one antibiotic to the DNA duplex d(GCGAATTCGC)$_2$ was measured by calorimetry: At 27°C, ΔH° = -63 kJ/mol and ΔS° = -50 J/mol K.

(a) Assuming only one binding site per DNA duplex molecule, calculate the binding constant (K_b) at 27°C.

(b) Calculate the concentration of free antibiotic at which equal amounts of DNA/antibiotic complex and free DNA are present.

[hint: $Ab + DNA \xleftrightarrow{K_b} Ab \cdot DNA$] (15%)