國立成功大學 104 學年度碩士班招生考試試題

系所組別：化學系甲組

考試科目：物理化學

考試日期：0212，節次：1

※ 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。

說明: 1. 請依題序作答並標明題號。第二部分計算題需寫出計算過程，只寫答案不給分 。

2. **R= 8.314 J K^{-1} mol^{-1} = 0.082 atm L K^{-1} mol^{-1}**

(一)單選題 10 題，每題 6 分，共 60 分，答錯倒扣 1 分

(1) Consider a regular solution made of liquid A and B, where $\ln \gamma_A = 5x_B^2$ and $\ln \gamma_B = 5x_A^2$. Calculate H^E (in nRT) at $x_A = 0.3$.
(A)0.21 (B)0.38 (C)0.63 (D)0.84 (E)1.05

(2) A certain gas obeys the equation of state P(V-nb)=nRT, where b and R are constants. If the pressure and temperature are such that $V_m = 5$ b, calculate $\ln\phi$, where ϕ is the fugacity coefficient.
(A)0.18 (B)0.25 (C)0.29 (D)0.34 (E)0.38

(3) Express $(\partial H/\partial P)_T$ in terms of T, V, and α.
(A)V(1+ Tα) (B)T(1- Vα) (C)V/(1- Tα) (D)V(1- Tα) (E)V/(Tα−1)

(4) At 25 °C, the density of a 50 % by mass ethanol-water solution is 0.914 g/cm^3. Given that the partial molar volume of water in the solution is 17.4 cm^3/mol, calculate the partial molar volume (in cm^3/mol) of the ethanol.
(A)56.3 (B)32.5 (C)57.4 (D)41.6 (E)48.5

(5) The normalized wave functions for a particle confined to move on a circle are $\psi(\phi) = (1/2\pi)^{1/2} e^{-im\phi}$, where m =0, ±1, ±2,...and $0 \leqq \phi \leqq 2\pi$. Determine $<\phi>$.
(A)0 (B)π/2 (C)π (D)5π/4 (E)3π/2

(6) A particle is in a state described by the wave function $\psi(x) = (2a)^{1/2} e^{-ax}$, where a is a constant and $0 \leqq x \leqq \infty$. Determine the expectation value of the commutator of the position and momentum operators.
(A)0 (B)$i\hbar$ (C)-$i\hbar$ (D)$i\hbar$/2 (E)-2$i\hbar$

(7) Suppose that an atom has 3 electrons in different orbitals. What are the possible values of the total spin quantum number S?
(A)3/2, 1/2, 1/2 (B)1, 0, 3/2 (C)3/2, 1/2, 0 (D)1, 0, 1/2 (E)3/2, 1, 1/2

(8) How many of the following transitions are allowed in the normal electronic emission spectrum of a many-electron atom: (a) $^3D_2 \rightarrow {}^3P_1$, (b) $^3P_2 \rightarrow {}^1S_0$, (c) $^3F_4 \rightarrow {}^3D_3$, (d) $^3P_{3/2} \rightarrow {}^2S_{1/2}$, (e) $^3D_3 \rightarrow {}^1P_1$?
(A)0 (B)1 (C)2 (D)3 (E)4

(9) Consider the dimerization $2A \rightleftharpoons A_2$ with the forward rate constant k_1 and backward rate constant k_2. What's the expression of the relaxation time?
(A)$(k_1+4k_2[A]_{eq})^{-1}$ (B)$(k_2-4k_1[A]_{eq})^{-1}$ (C)$(k_2+4k_1[A]_{eq})^{-1}$ (D)$(k_2+2k_1[A]_{eq})^{-1}$ (E)$(4k_2-k_1[A]_{eq})^{-1}$

(10) The diffusion coefficient of I_2 in hexane at 25 °C is 4.05×10^{-9} m^2 s^{-1}. Estimate the time (in s) required for an iodine molecule to have a root mean square displacement of 1.0 cm.

(A)1.2×10^4 (B)2.2×10^3 (C)2.4×10^4 (D)7.3×10^3 (E)4.1×10^3

(二)計算題 3 題，共 40 分

(1) The cycle involved in the operation of an internal combustion engine is called the Otto cycle. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A.

(a)Derive an expression for the efficiency of the cycle in terms of T_A, T_B, T_C, and T_D, assuming that the heat is supplied in Step 2. (6%)

(b)Same as (a), but in terms of V_A and V_B. (5%)

(c)Determine the changes in entropy of the system in step 2 and 4, respectively. Assume that in state A, V = 4.00 dm^3, p = 1.00 atm, and T = 300 K, that $V_A = 10V_B$, $p_C/p_B = 5$, and that $C_{p,m}$=7/2 R. (4%)

(2) Write down the secular determinant for linear H_3 within the Huckel approximation, and estimate the binding energy. (12%)

(3) Consider the formation and decay of an excited singlet state:

Absorption	$S + h\nu_i \rightarrow S^*$	absorbation rate I_{abs}
Fluorescence	$S^* \rightarrow S + h\nu_f$	rate constant k_f
Internal conversion	$S^* \rightarrow S$	rate constant k_{IC}
Intersystem crossing	$S^* \rightarrow T^*$	rate constant k_{ISC}
Quenching	$S^* + Q \rightarrow S + Q$	rate constant k_Q

(a)Derive the expression of the fluorescence quantum yield ϕ_f. (8%)

(b)Obtain the ratio $\phi_{f,o}/\phi_f$, where $\phi_{f,o}$ is measured in the absence of a quencher Q. (5%)