國立成功大學
111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

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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。

說明：1. 請依題序作答並標明題號

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

(一)單選題12題，每題5分，共60分，不倒扣。

(1) The pressure on a block of copper at a temperature of 300 K is increased isothermally and reversibly from 1 to 1000 bar. Assume that α, κ and density are constant and equal to $5\times10^{-5}\ K^{-1}$, $9\times10^{-12}\ m^2/N$, and $9\times10^3\ kg/m^3$, respectively. Calculate the work done (in J) on the copper per kilogram.

(A)5 (B)12 (C)8 (D)2 (E)15

(2) Calculate the change of entropy (in J/K) on the copper per kilogram in Problem 1.

(A)-1.45 (B)-0.56 (C)-0.72 (D)-0.32 (E)-1.85

(3) Apply L'Hopital's rule to the Clapeyron equation either respect to P or T to obtain the second-order phase transition temperature.

(A)$V\Delta C_p\Delta\alpha/\Delta\kappa$ (B)$(\Delta\alpha)/(V\Delta C_p\Delta\kappa)$ (C)$V(\Delta\kappa)^2/(\Delta C_p\Delta\alpha)$ (D)$\Delta C_p\Delta\kappa/[V(\Delta\alpha)^2]$
(E)$\Delta C_p\Delta\kappa/[V(\Delta\alpha)]$

(4) A container is divided into two compartments. One contains 2.0 mole H_2 at 2.0 atm and 25 °C; the other contains 2.0 mole N_2 at 3.0 atm and 25 °C. Calculate the Gibbs free energy of mixing (in 596R) when the partition of the container is removed. Assume that the gases are perfect.

(A)ln(1.56) (B)ln(0.45) (C)ln(0.66) (D)ln(2.20) (E)ln(0.24)

(5) Consider the reaction

$$A + B \rightleftharpoons P \qquad \text{(rate constant: forward } k_1\text{, backward } k_{-1}\text{)}$$

, where $[A]_o = [B]_o$. A temperature jump experiment is performed where the relaxation time constant is measured to be 5.0×10^{-4}, resulting an equilibrium where $K_{eq} = 1.0$ with $[P]_{eq} = 0.25$ M. Derive an expression of relaxation time.

(A)$[k_1([A]_{eq} + [B]_{eq}) - k_{-1}[P]_{eq}]^{-1}$ (B)$k_1([A]_{eq} + [B]_{eq}) - k_{-1}$ (C)$[k_1([A]_{eq} + [B]_{eq}) + k_{-1}]^{-1}$
(D)$[k_{-1}([A]_{eq} + [B]_{eq}) + k_1[P]_{eq}]^{-1}$ (E)$[k_1([A]_{eq} + [B]_{eq}) - k_{-1}]^{-1}$

(6) Calculate k_{-1} (in $10^3\ s^{-1}$) in Problem 5.

(A)1.0 (B)1.5 (C)0.8 (D)2.2 (E)2.5

(7) Consider the reaction $A \rightarrow P$ with rate equation $d[P]/dt = k[A]^n$. Calculate the half-life.

(A)$2^{n-1}/(n-1)k[A]_o^{n-1}$ (B)$(2^{n-1}-1)/(n-1)k[A]_o^{n-1}$ (C)$k(2^n-1)/(n-1)[A]_o^{n-1}$
(D)$(2^{n-1}-1)/(n-1)k[A]_o^n$ (E)$(2^{n-1}-1)/(n)k[A]_o^{n-1}$

(8) The reaction $2\,F_2O\,(g) \rightarrow 2\,F_2\,(g) + O_2(g)$ is believed to follow the mechanism:

(1) $2\,F_2O \rightarrow F + OF + F_2O$ rate constant k_1
(2) $F + F_2O \rightarrow F_2 + OF$ rate constant k_2
(3) $2\,OF \rightarrow O_2 + 2F$ rate constant k_3
(4) $2\,F + F_2O \rightarrow F_2 + F_2O$ rate constant k_4

Use the steady state approximation to obtain the expression of [F].

(A)$(k_1[F_2O]/k_4)^{1/2}$ (B)$(k_2[F_2O]/k_3)^{1/2}$ (C)$(k_1[F_2O]/k_4)^{3/2}$ (D)$k_2[F_2O]^{1/2}/k_4$ (E)$(k_1)^{1/2}[F_2O]/(k_3)^{1/2}$

(9) The mechanism in Problem (8) can be shown to be consistent with the experimental rate law $-d[F_2O]/dt = k_a [F_2O]^2 + k_b [F_2O]^3$. What is k_b?

(A)$(k_2k_1/k_3)^{1/2}$ (B)$k_3(k_1/k_4)^{1/2}$ (C)$k_4^{1/2}k_1/k_3$ (D)$k_2(k_1/k_4)^{1/2}$ (E)$k_1(k_2/k_4)^{1/2}$

(10) The schrodinger equation for a particle of mass m moving in a ring of radius r in the xy-plane with zero potential energy is $-(h^2/8\pi^2 I)d^2\psi(\phi)/d\phi^2 = E\psi(\phi)$, were $I = mr^2$. What's the normalization constant of the wavefunction?

(A)$\pi^{-1/2}$ (B)$(2\pi)^{-1/2}$ (C)$(2\pi)^{-1}$ (D)2π (E)π^2

(11) Calculate the expectation value of the angular momentum in Problem 10 represented by the operator $(h/2\pi i)d/d\phi$ if the quantum number is equal to 4?

(A)$h/8\pi$ (B) $(h/\pi)^2$ (C)$h/2\pi$ (D)$(h/2\pi)^2$ (E)$2h/\pi$

(12) How many of the following molecules (H_2, HCl, CO_2, H_2O, CH_3CH_3, N_2, CH_4, CH_3Cl) may show infrared absorption spectra?

(A)4 (B)5 (C)6 (D)7 (E)8

(二)非選擇題 3 題，共 40 分，需寫出計算過程，只寫答案不給分。

(1) Consider a system of particle in a cubic box at certain temperature T_1, where the energy level is given by $E_n = n^2h^2/(8ma^2)$. Work is done on this system adiabatically and reversibly so that the length of box, a, is reduced to $2^{-1/2}$ of its original length.

(a)Calculate the final temperature. (6 %)

(b)What's the effect on the molecular partition function? (5 %)

(c)What's the effect on the occupations of the energy levels? (5 %)

(2) The number of configurations available to a polymer network can be shown to be

$$W = C \exp[-a(L_x^2 + L_y^2 + L_z^2)]$$

, where C and a are constant, and L_x, L_y, L_z are extension ratios in the x, y, and z directions. For an ideal rubber, dW = -f dl and dV= 0 in the stretching process. Let $L_x = L_y$, and $L_z = l/l_o = \lambda$, where l and l_o are initial and final sample length.

(a)Derive the entropy of the system as a function of λ. (8 %)

(b)Use the relation $f = -T(\partial s/\partial l)_T$ to derive the expression of the restoring force f as a function of λ and T. (6 %)

(3) Suppose the ground vibrational state of a molecule is modelled by using the particle in a box wavefunction $\psi_o = (2/L)^{1/2}\sin(\pi x/L)$ for $0 \le x \le L$ and 0 elsewhere. Calculate the Frank-Condon factor for a transition to a vibrational state described by $\psi' = (2/L)^{1/2}\sin[(\pi(x-L/2)/L]$ for $L/2 \le x \le 3L/2$ and 0 elsewhere. (10 %)