# 國立成功大學 107 學年度碩士班招生考試試題

系　　所：化學系

考試科目：物理化學　　考試日期：0206，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**

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

**(一)單選題 14 題，每題 5 分，共 70 分，不倒扣。**

(1) By how much (in J/mol) does the chemical potential of super-cooled water at -10 °C exceed that of ice? The heat of freezing is -6.01 x $10^3$ J/mol at 0 °C, and $C_{p,s}$- $C_{p,l}$ is -37.3 J/K, mol.
(A)22 (B)132 (C)220 (D)245 (E)342

(2) Express $\mu_J C_V$ as a function of P, T, α, and κ, where the Joule coefficient $\mu_J$ is defined as $(\partial T/\partial V)_U$.
(A)P- (αT/κ) (B)P+ (κ/αT) (C)P+ (αT/κ) (D)-P+ (κ/αT) (E)P- (κ/αT)

(3) Calculate the energy that must be transferred as heat for a gas with equation of state $PV_m/RT = 1 + B/V_m$ that expands reversibly and isothermally from $V_1$ to $V_2$.
(A)nRT [ln($V_2/V_1$)- B($V_2^{-1}$- $V_1^{-1}$)] (B)nRT [ln($V_2/V_1$)- nB($V_2^{-1}$- $V_1^{-1}$)]
(C)nRT [ln($V_2/V_1$)+ nB($V_2$- $V_1$)] (D)nRT [ln($V_2/V_1$)+ B($V_2^{-1}$- $V_1^{-1}$)]
(E)nRT [ln($V_2/V_1$)- nB($V_2$- $V_1$)]

(4) Assuming that at 300 K $\Delta G_f^o$ for Fe(g) is 360 kJ/mol, $\Delta H_f^o$ for Fe(g) is 400 kJ/mol, and $\Delta H_f^o$ is constant, calculate $\Delta G_f^o$ (in kJ/mol ) at 400 K.
(A)356 (B)372 (C)390 (D)416 (E)442

(5) Benzene and toluene form nearly ideal solutions. Consider an equimolar solution of benzene and toluene. At 20°C the vapour pressures of pure benzene and toluene are 10.0 kPa and 3.0 kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure. Calculate the vapour pressure (in kPa) when only a few drops of liquid remain.
(A)3.0 (B)3.5 (C)4.0 (D)4.6 (E)6.5

(6) The standard enthalpies of formation of Na(g) and $Na^+$(g) at 300 K are 107 kJ/mol and 609 kJ/mol, respectively. Estimate the first ionization energy (in kJ/mol) of Na(g).
(A)502 (B)490 (C)508 (D)514 (E)496

(7) Evaluate the z-component of the angular momentum of a particle on a ring that is described by the wave function cos ϕ
(A)0 (B)h/(2π) (C)-h/π (D)2h/π (E)-h/(2π)

(8) What's the kinetic energy in Problem 7 if the wave function is $e^{-2i\phi}$ ?
(A)$h^2/(2\pi^2 I)$ (B)$h^2/(4\pi^2 I)$ (C)$h^2/(\pi^2 I)$ (D)$h^2/(8\pi^2 I)$ (E)$2h^2/(\pi^2 I)$

(9) Evaluate the commutator $[\hat{H}, \hat{x}]$, where $\hat{H} = \hat{p}_x^2/(2m) + V$. (V is a constant)
(A)$ih\hat{p}_x/(2\pi m)$ (B)$-ih\hat{p}_x/(2\pi m)$ (C)$ih\hat{p}_x/(\pi m)$ (D)$-2ih\hat{p}_x/(\pi m)$ (E)$-ih\hat{p}_x/(\pi m)$

(10)Consider a one-dimensional random walk of 10 steps, beginning from the origin. What's the probability that the drunker will have moved 2 steps to the right of origin?
(A)0.04 (B)0.08 (C)0.12 (D)0.21 (E)0.25

(11)Consider a consecutive unimolecular reaction $A \rightarrow B \rightarrow P$, where the rate constants are $k_a$ and $k_b$, respectively. What's the expression of [B]?
(Note: The solution of $df/dx + a(x)f = b(x)$ is $g(x)^{-1}[\int b(x)\, g(x)\, dx + C]$, where $g(x) = \exp(\int a(x)\, dx)$)
(A)$k_a[A]_o[\exp(-k_at) - \exp(-k_bt)]/(k_a-k_b)$ (B)$k_a[A]_o[\exp(-k_at) - \exp(-k_bt)]/(k_b-k_a)$
(C)$k_a[A]_o[\exp(-k_at) - \exp(-k_bt)]/(k_a+k_b)$ (D)$k_b[A]_o[\exp(-k_at) + \exp(-k_bt)]/(k_b-k_a)$
(E)$k_a[A]_o[\exp(-k_at) + \exp(-k_bt)]/(k_a-k_b)$

(12)What's the maximum concentration of B in Problem 11 if $k_b = 2\, k_a$?
(A)$(2/3)[A]_o$ (B)$[A]_o/5$ (C)$[A]_o/3$ (D)$[A]_o/2$ (E)$[A]_o/4$

(13)How much time is required to reach $[B]_{max}$ in Problem 11 if $k_b = k_a$?
(A)$2/k_a$ (B)$4/k_a$ (C)$1/k_a$ (D)$3/k_a$ (E)$2/(3k_a)$

(14)For a second-order reaction of the form $A \rightarrow n\, B$, with rate constant k, derive the concentration of B as a function of time.
(A)$nkt[A]_o^2/(1+ kt[A]_o)$ (B)$n[A]_o/[1- \exp(-kt)]$ (C)$nkt[A]_o/(1+ kt)$
(D)$nkt[A]_o^2/(kt[A]_o-1)$ (E)$n[A]_o/[1+ \exp(-kt)]$

**(二)計算題 2 題，共 30 分，需寫出計算過程，只寫答案不給分。**

(1) Consider a system of N molecules with energy levels $\varepsilon_n = n\varepsilon$, where n is an integer, with value $0 \sim 4$.
(a)Derive the expression of mean energy $\langle\varepsilon\rangle$, and evaluate its value as $T \rightarrow \infty$.
(b)Calculate the fraction of molecules at n=4 as $T \rightarrow \infty$. (14 %)

(2) Write down the secular determinant for cyclobutadiene by using Huckel approximation, and solve for the roots of the secular equation to obtain the total π-bond energy. What's the delocalization energy? (16 %)