

國立成功大學  
110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

日 期： 0203

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

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

(一) 單選題 14 題，每題 5 分，共 70 分，不倒扣。

(1) A scientist proposed the following equation of state

$$P = RT/V_m - B/V_m^2 + C/V_m^3$$

What's the critical temperature?

(A)  $C/(2RB^2)$  (B)  $C^2/(4RB)$  (C)  $CR/(3B^2)$  (D)  $B^2R/(4C)$  (E)  $B^2/(3RC)$

(2) What's the equation of state in reduced variables for Problem 1?

(A)  $P_r = 2T_r V_r^{-1} - V_r^{-2} + V_r^{-3}$  (B)  $P_r = T_r V_r^{-1} - 3V_r^{-2} + 2V_r^{-3}$  (C)  $P_r = T_r V_r^{-1} - 2V_r^{-2} + 3V_r^{-3}$   
(D)  $P_r = 3T_r V_r^{-1} - 3V_r^{-2} + V_r^{-3}$  (E)  $P_r = 4T_r V_r^{-1} - 2V_r^{-2} + 3V_r^{-3}$

(3) Arrange the following ions in aqueous solution in order of increasing standard molar entropy: (1)  $H^+$  (2)  $Na^+$  (3)  $Cu^{+2}$  (4)  $Li^+$

(A) 1, 4, 2, 3 (B) 3, 4, 2, 1 (C) 3, 1, 4, 2 (D) 2, 4, 1, 3 (E) 3, 2, 1, 4

(4) Consider a 2-level system with energy  $\varepsilon_2 = 2\varepsilon_1$  and  $g_2 = 2g_1$ , where  $g_i$  is the degeneracy of level  $i$ . What value of  $T$  is required to obtain a population ratio ( $n_2/n_1$ ) of 0.5?

(A)  $\varepsilon_1/(k_B \ln 2)$  (B)  $\varepsilon_1/(2k_B \ln 5)$  (C)  $(\varepsilon_1 \ln 2)/(2k_B)$  (D)  $\varepsilon_1/(2k_B \ln 2)$  (E)  $2\varepsilon_1/(k_B \ln 5)$

(5) The equilibrium constant of the reaction  $2 C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$  is found to fit the expression  $\ln K = A + B/T + C/T^2$  between 300 K and 600 K, with  $A = -1.0$ ,  $B = -1100 \text{ K}$ , and  $C = 2.0 \times 10^5 \text{ K}^2$ . Calculate the standard reaction enthalpy (in R) at 400 K.

(A) 60 (B) 100 (C) 125 (D) 135 (E) 160

(6) What is the expectation value of  $\langle x \rangle$  for a quantum mechanical harmonic oscillator in the ground state, with  $\Psi = (4\alpha^3/\pi)^{1/4} x \exp(-\alpha x^2/2)$ ? ( $\int \exp(-ax^2) dx = (\pi/a)^{1/2}$ ,  $\int x^4 \exp(-ax^2) dx = (3/4) (\pi/a^5)^{1/2}$ , where both are integrated from  $-\infty$  to  $\infty$ .)

(A)  $3\alpha/4$  (B) 0 (C)  $\alpha^{-1/2}$  (D)  $2\alpha^{-3/2}$  (E)  $3\alpha^{-1/2}/4$

(7) What is the standard deviation  $\Delta x$  in Problem 6?

(A)  $(3/2\alpha)^{1/2}$  (B) 0 (C)  $3/(4\alpha^{3/2})$  (D)  $2\alpha^{-3/2}$  (E)  $3/(2\alpha^{1/2})$

(8) How many transitions below ( ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ ,  ${}^3P_0 \rightarrow {}^3S_1$ ,  ${}^3D_3 \rightarrow {}^1P_1$ ,  ${}^3P_2 \rightarrow {}^1S_0$ ,  ${}^3F_4 \rightarrow {}^3D_3$ ) are allowed in the electronic emission spectrum of a many-electron atom?

(A) 1 (B) 2 (C) 3 (D) 4 (E) 5

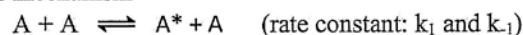
(9) Which of the following term symbols is possible for Sc  $[Ar]3d^14s^2$ ?

(A)  ${}^2D_2$  (B)  ${}^3P_2$  (C)  ${}^2S_0$  (D)  ${}^2D_{5/2}$  (E)  ${}^1P_1$

- (10) For the gas-phase reaction  $A + A \rightarrow A_2$ , the experimental rate constant  $k_2$  has been fitted to the Arrhenius equation with the pre-exponential factor of  $5.0 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  at 300 K and its activation energy is 65.0 kJ/mol. What's the enthalpy of activation (in kJ/mol)?

(A)62.5 (B)63.8 (C)58.5 (D)56.2 (E)60.0

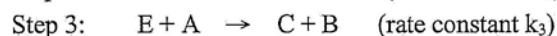
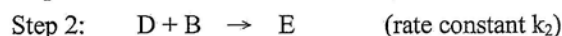
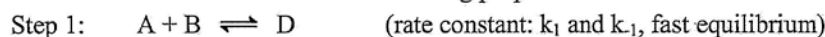
- (11) For the mechanism



If  $k_{-1}[A] \gg k_2$ , what's  $d[P]/dt$ ?

(A) $2k_{-1}k_2[A]/k_1$  (B) $2k_1k_2[A]/k_{-1}$  (C) $2k_1k_{-1}[A]/k_2$  (D) $k_{-1}k_2[A]/k_1$  (E) $k_1^2k_2[A]/k_{-1}$

- (12) The reaction  $2A + B \rightarrow C$  has the following proposed mechanism:



If step 2 is the rate-determining step, what should be the rate of formation of C?

(A) $k[A]$  (B) $k[A]^2[B]$  (C) $k[A][B]^2$  (D) $k[A][B]$  (E) $k[A]^2[B]^2$

- (13) A nitrogen molecule with mass  $m$  is confined in a cubic box of volume  $1.0 \text{ m}^3$ .

Assuming that the molecule has an energy equal to  $3kT/2$ , what's the de Broglie wavelength of the molecule?

(A) $h/(mkT)^{3/2}$  (B) $h/(2mkT)^{3/2}$  (C) $h^2/(mkT)$  (D) $(2mkT)^{1/2}/h$  (E) $h/(3mkT)^{1/2}$

- (14) The half-lives for the forward and reverse reactions that are first orders in both directions are 20 ms and 40 ms, respectively. Calculate the corresponding relaxation time (in ms) for return to equilibrium after a temperature jump.

(A) $40/(3\ln 2)$  (B) $15/(2\ln 2)$  (C) $20/(3\ln 2)$  (D) $(20\ln 2)/3$  (E) $15/\ln 2$

(二)非選擇題 2 題，共 30 分，需寫出計算過程，只寫答案不給分。

(1) A certain gas obeys the following equation of state:

$$PV_m = RT + bP - aP/(RT)$$

(a) Calculate its Joule-Thompson coefficient.

(b) Calculate  $\Delta S$  for n mole gas expanding isothermally and reversibly from  $P_1$  to  $P_2$ .

(14 %)

(2) Evaluate the commutators (a)  $[\hat{H}, \hat{p}_x]$  and (b)  $[\hat{H}, x]$ , where  $\hat{H} = p_x^2/(2m) + (1/2)kx^2$ .

(16 %)