

系所組別： 化學系

考試科目： 物理化學

考試日期： 0226，節次： 1

※ 考生請注意：本試題可使用計算機，並限「考選部核定之國家考試電子計算器」機型

說明： 1. 請依題序作答並標明題號，計算題需寫出計算過程，只寫答案不給分  
2.  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ atm L K}^{-1} \text{ mol}^{-1}$ ,  $h = 6.626 \times 10^{-34} \text{ Js}$

(一)單選題 12 題，每題 6 分，共 72 分，答錯倒扣 1 分

- (1) 3.0 mole of ideal gas ( $C_{v,m} = 3R/2$ ) at  $25^\circ\text{C}$  and  $10.0 \text{ atm}$  expands adiabatically and irreversibly against a constant  $1.0 \text{ atm}$  pressure. What's the final temperature (in K)?  
(A)190.7 (B)212.4 (C)226.5 (D)232.8 (E)238.5
- (2) Consider a system of  $N$  molecules with energy levels  $\epsilon_n = n\epsilon$ , where  $n$  is an integer, with value  $0 \sim 10$ . What's the fraction of molecules staying at the ground state at  $T = \infty$ ?  
(A)0 (B)0.09 (C)0.17 (D)0.22 (E)0.30
- (3) If  $10.9 \text{ kJ}$  of heat is released when  $2.0 \text{ mole}$  of supercooled water at  $-15.0^\circ\text{C}$  and  $1.0 \text{ atm}$ . freezes, calculate  $\Delta S_{\text{sys}}$  (in  $\text{J/mol, K}$ ) for the fusion (熔解) of ice at  $-15^\circ\text{C}$ . Assume the molar heat capacities for  $\text{H}_2\text{O(s)}$  and  $\text{H}_2\text{O(l)}$  are  $37.5$  and  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, and are temperature independent.  
(A)22.1 (B)21.1 (C)25.2 (D)30.1 (E)19.9
- (4) Express  $(\partial P/\partial S)_V$  in terms of  $T$ ,  $C_v$ ,  $\kappa$ , and  $\alpha$ .  
(A) $\alpha\kappa C_v/T$  (B) $T\alpha C_v/\kappa$  (C) $\alpha C_v/T\kappa$  (D) $T\alpha/C_v\kappa$  (E) $T\kappa/\alpha C_v$
- (5) The partial molar volume of  $\text{K}_2\text{SO}_4(\text{aq})$  at  $298 \text{ K}$  is given by  
 $V_B/(\text{cm}^3 \text{ mol}^{-1}) = 32.280 + 18.216 (m/m^0)^{1/2}$   
where  $m$  is the molality of  $\text{K}_2\text{SO}_4$ . If the molar volume of pure water at  $298 \text{ K}$  is  $18.079 \text{ cm}^3/\text{mol}$ , calculate the partial molar volume (in  $\text{cm}^3/\text{mol}$ ) of water at  $m = 1.0 \text{ mol/Kg}$ .  
(A)16.25 (B)17.18 (C)17.56 (D)17.97 (E)18.03
- (6) A particle is in a state described by the wave function  $\psi = (\cos a)e^{ikx} + (\sin a)e^{-ikx}$ , where  $a$  is a parameter. What's the value of  $\cos a$  if it were 70 % certain that the particle had linear momentum  $-k\hbar$ ?  
(A)0.548 (B)0.837 (C)0.707 (D)0.3 (E)0.866
- (7) What's the expectation value of linear momentum (in  $k\hbar$ ) in Problem 6?  
(A)0.3 (B)-0.7 (C)-0.4 (D)-0.3 (E)1.2
- (8) Determine the commutator of the operators  $d^2/dx^2$  and  $x^2$ .  
(A)2x (B)4 (C)2 (D)4x (E)6
- (9) Which term is likely to lie lowest in energy for the configuration  $np^1nd^1$ ?  
(A) $^3F_4$  (B) $^3F_2$  (C) $^3P_2$  (D) $^1D_2$  (E) $^1P_1$

(背面仍有題目,請繼續作答)

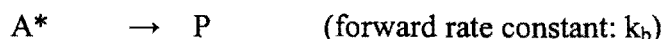
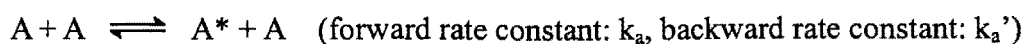
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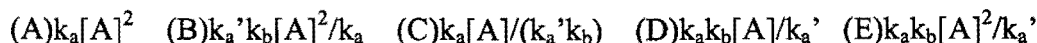
考試日期：0226，節次：1

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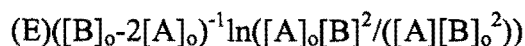
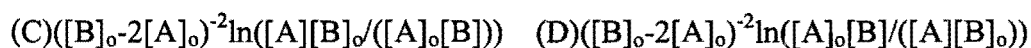
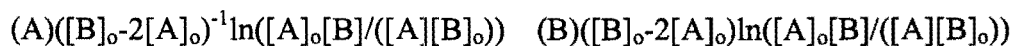
(10) Consider the reaction mechanism



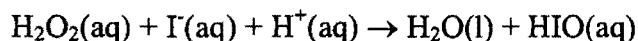
If  $k_a'[A] \gg k_b$ , derive the expression of  $d[P]/dt$ .



(11) Consider the reaction  $A + 2B \rightarrow P$ , where  $\text{rate} = k_r[A][B]$  and  $[B]_0 \neq 2[A]_0$ . Which of the following is a correct expression of  $k_r t$ ?



(12) At 25 °C, the rate constant  $k$  of the reaction



is  $12.2 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$  at an ionic strength of 0.0525. What would happen to the rate constant as the ionic strength decreases?

(A)  $k$  decreases. (B)  $k$  increases. (C)  $k$  stays the same (D)  $k$  increases first and then decreases. (E) cannot be judged.

(二) 計算題 2 題，共 28 分

(13) Consider a van der Waals gas with  $a = 3.61 \text{ atm L}^2/\text{mol}^2$  and  $b = 0.0429 \text{ L/mol}$ .

(a) Estimate the Boyle temperature (in K).

(b) Calculate  $\Delta H_m$  (in kJ/mol) when the pressure on the gas is decreased from 200.0 atm to 1.0 atm at 300 K. (Note:  $C_{p,m} = 7R/2$ ,  $\mu = [(2a/RT) - b]/C_{p,m}$ ) (14%)

(14) The hamiltonian for a point mass of  $m$  rotates in a cycle (with  $V=0$ ) can be simplified as

$\hat{H} = -(\hbar^2/2I)d^2/d\phi^2$ , where  $I = mr^2$ , and  $\phi$  is the azimuthal angle. Derive the normalized

general solution and the energy in terms of quantum number. (14%)