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 J K^{-1} mol^{-1} = 0.082 atm L K^{-1} mol^{-1}, h=6.626x10^{-34} 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 °C and 10.0 atm expands adiabatically and irreversibly against a constant 1.0 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 ε_n= nε, where n is an integer, with value 0 ~ 10. What's the fraction of molecules staying at the ground state at T =∞?
(A)0 (B)0.09 (C)0.17 (D)0.22 (E)0.30

(3) If 10.9 kJ of heat is released when 2.0 mole of supercooled water at -15.0°C and 1.0 atm. freezes, calculate ΔS_{sys} (in J/mol, K) for the fusion (熔解) of ice at -15 °C. Assume the molar heat capacities for H_2O(s) and H_2O(l) are 37.5 and 75.3 J K^{-1} 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, κ, and α.
(A)ακC_v/T (B)TαC_v/κ (C)αC_v/Tκ (D)Tα/C_vκ (E)Tκ/αC_v

(5) The partial molar volume of K_2SO_4(aq) at 298 K is given by

$$V_B/(cm^3\ mol^{-1}) = 32.280 + 18.216\ (m/m^o)^{1/2}$$

,where m is the molality of K_2SO_4. If the molar volume of pure water at 298 K is 18.079 cm^3/mol, calculate the partial molar volume (in cm^3/mol) of water at m= 1.0 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 –kħ?
(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 kħ) 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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(10) Consider the reaction mechanism

$A + A \rightleftharpoons A^* + A$ (forward rate constant: k_a, backward rate constant: k_a')

$A^* \rightarrow P$ (forward rate constant: k_b)

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

(A)$k_a[A]^2$ (B)$k_a'k_b[A]^2/k_a$ (C)$k_a[A]/(k_a'k_b)$ (D)$k_ak_b[A]/k_a'$ (E)$k_ak_b[A]^2/k_a'$

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

(A)$([B]_o-2[A]_o)^{-1}\ln([A]_o[B]/([A][B]_o))$ (B)$([B]_o-2[A]_o)\ln([A]_o[B]/([A][B]_o))$

(C)$([B]_o-2[A]_o)^{-2}\ln([A][B]_o/([A]_o[B]))$ (D)$([B]_o-2[A]_o)^{-2}\ln([A]_o[B]/([A][B]_o))$

(E)$([B]_o-2[A]_o)^{-1}\ln([A]_o[B]^2/([A][B]_o^2))$

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

$$H_2O_2(aq) + I^-(aq) + H^+(aq) \rightarrow H_2O(l) + HIO(aq)$$

is 12.2 $L^2\ mol^{-2}\ min^{-1}$ 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 atm L^2/mol^2 and b= 0.0429 L/mol.

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

(b)Calculate ΔH_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 ϕ is the azimuthal angle. Derive the normalized general solution and the energy in terms of quantum number. (14%)