國立臺灣大學110學年度碩士班招生考試試題 題號: 281

科目:物理化學(A)(基礎熱力學與反應動力學)

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第一部分 單選題(1-14),每題 5 分,共 70 分 ※注意:請於試卷首頁「選擇題 作答區」作答。

- 1. NH₄Cl when dissolved in water leads to cooling sensation. The dissolution of NH₄Cl at constant temperature is accompanied by (A) increase in entropy, (B) decrease in entropy, (C) no change in entropy, (D) no change in enthalpy, (E) decrease in free energy.
- 2. Heat energy of 743 J is needed to raise the temperature of 5 moles of an ideal gas by 2 K at constant pressure. How much heat is needed to raise the temperature of the same mass of the gas by 2 K at constant volume? (A) 826 J, (B) 743 J, (C) 660 J, (D) 600 J, (E) 545 J.
- 3. Three samples of the same ideal gas (the ratio of heat capacities $\gamma = 1.5$) have equal volumes and temperatures. The volume of each sample is doubled, the process being isothermal, adiabatic, and isobaric, respectively. If the final pressures are equal for the three samples, the ratio of their initial pressure is (A) 1:1:1, (B) 2:2:1, (C) 1:2:1, (D) 2:2 $\sqrt{2}$:1, (E) 1:2 $\sqrt{2}$:2.
- 4. A sample of ideal gas that initially occupies 15.0 L at 300 K and 1.0 bar is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by 5.0 J/K? (A) 5.40 L, (B) 5.56 L, (C) 8.22 L, (D) 20.6 L, (E) 40.5 L.
- 5. The specific heats of iodine vapor and solid are 0.031 and 0.055 cal/g, respectively. If the enthalpy of sublimation of iodine is 24.0 cal/g at 200 °C, the enthalpy of sublimation of iodine at 250 °C should be (A) 24.0 cal/g, (B) 26.4 cal/g, (C) 20.8 cal/g, (D) 28.6 cal/g, (E) 22.8 cal/g.
- 6. A solution was prepared by dissolving 7.45 g of KCl in 200 g of H₂O in a calorimeter with a water equivalent of 25 g. The temperature of the water had reduced from 28 °C to 25 °C. ΔH for dissolving KCl in water is (Specific heat capacity of water is 4.2 J/K/g.) (A) 2.520 kJ/mol, (B) 2.835 kJ/mol, (C) 20.60 kJ/mol, (D) 25.20 kJ/mol, (E) 28.35 kJ/mol.
- 7. The molar enthalpy of vaporization of benzene at boiling point (353 K) is 7.4 kcal/mol. The molar internal energy change of vaporization is (A) 7.400 kcal/mol, (B) 8.106 kcal/mol, (C) 6.694 kcal/mol, (D) 62.47 kcal/mol, (E) 70.86 kcal/mol.
- 8. At 200 °C, PCl₅ dissociates as follows: PCl₅(g) ≠ PCl₃(g) + Cl₂(g). It was found that the equilibrium vapors are 62 times as heavy as hydrogen. The percentage dissociation of PCl₅ at 200 °C is (A) 34.1%, (B) 68.1%, (C) 40.5%, (D) 70.3%, (E) 50.6%.
- 9. The Deacon reaction is the oxidation of HCl by O₂: HCl(g) + 1/4 O₂(g) $\rightleftharpoons 1/2$ Cl₂(g) + 1/2 H₂O(g). At a pressure of 730 mm and with an initial mixture containing 8% HCl and 92% O2, the degree of decomposition of the HCl is 0.08. What is the equilibrium partial pressure of oxygen? (A) 566.84 mm, (B) 671.60 mm, (C) 659.92 mm, (D) 537.28 mm, (E) 670.43 mm.
- 10. The standard free energy of formation Δ_fG° are 30.426 kJ/mol for trans-1,2-dichloroethene and 22.112 kJ/mol for cis-1,2-dichloroethane at 27 °C. The molar ratio of urans and cis isomers at equilibrium at 27 °C is (A) 2:3, (B) 3:2, (C) 28:1, (D) 1:28, (E) 10:3.

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11. A quantity of 2 g of C₆H₅COOH dissolved in 25 g of benzene shows a depression in freezing point equal to 1.96 K. Molar depression constant for benzene is 4.9 K.kg/mol. What is the percentage association of acid if it forms double molecules (dimer) in solution? (A) 39%, (B) 78%, (C) 61%, (D) 19.5%, (E) 56%.

- 12. What is the order of a chemical reaction: $A + 2 B \rightarrow C$, if the rate formation of C increases by a factor of 2.82 on doubling the concentration of A and increases by a factor of 9 on tripling the concentration B? (A) 7/2, (B) 7/4, (C) 5/2, (D) 5/4, (E) 2.
- 13. Rate of the reaction: A → products is doubled when the concentration of A is increased four times. If the half-life of the reaction is 16 min, at a given concentration, then the time required for 75% of the reaction to complete is (A) 24.0 min, (B) 27.3 min, (C) 48.0 min, (D) 49.4 min, (E) 52.3 min.
- 14. Rate of an uncatalyzed first-order reaction at 300 K is half of the rate of catalyzed reaction at 150 K. If the catalyst lowers the threshold energy by 20 kcal, what is the activation energy of the uncatalyzed reaction? (A) 39.58 kcal/mol, (B) 19.58 kcal/mol, (C) 40.42 kcal/mol, (D) 20.42 kcal/mol, (E) 56.68 kcal/mol.

第二部分 非選擇題 (15-18), 共 30 分 ※注意:請於試卷上「非選擇題作答區」作答,並註明作答之題號。

- 15. A gas obeys the equation of state $V = RT/P + aT^2$ and its constant-pressure heat capacity is given by $C_p = A + BT + CP$, where a, A, B, and C are constants independent of T and P. Obtain expressions for (a) (6%) the Joule-Thomson coefficient and (b) (6%) its constant-volume heat capacity C_v .
- 16. (6%) The equilibrium $A \rightleftharpoons B$ is first-order in both directions. Derive an expression for the k' concentration of A as a function of time when the initial molar concentrations of A and B are $[A]_0$ and $[B]_0$.
- 17. (6%) Consider the following mechanism for the thermal decomposition of R2:
 - $(1) R_2 \stackrel{k_1}{\rightarrow} R + R$
 - $(2) R + R_2 \stackrel{k_2}{\rightarrow} P_B + R'$
 - $(3) R' \stackrel{k_3}{\rightarrow} P_A + R$
 - $(4) R + R \xrightarrow{k_4} P_A + P_B$

where R_2 , P_A , P_B are stable hydrocarbons and R and R' are radicals. Find the dependence of the rate of decomposition of R_2 on the concentration of R_2 .

18. (6%) The excess Gibbs energy of a certain binary mixture (A + B) is equal to gRTx(1 - x) where g is a constant and x is the mole fraction of a solute A. Find an expression for the chemical potential of A in the mixture. The chemical potential of pure A is μ_A *.

試題隨卷繳回