題號: 249 國立臺灣大學111學年度碩士班招生考試試題

科目:物理化學(A)

題號:249 共 2 頁之第 1 頁

節次: 7

第一部分 單選題 (1-15),每題 5分,共 75分 ※注意:請於試卷首頁「選擇題作答區」作答。

- 1. The internal energy of an ideal gas increases during an isothermal process when the gas is (A) expanded by adding more molecules to it, (B) expanded by adding more heat to it, (C) expanded against zero pressure, (D) compressed by doing work on it. (E) All of the above.
- 2. The latent heat of melting for a solid is 2930 J/mol. The entropy change for one mole of the solid melting at 300 K is (A) 9.77, (B) 20.73, (C) 2930, (D) 108.5, (E) 526.3 J/K/mol.
- 3. One mole of an ideal monoatomic gas is heated in a process  $PV^{5/2}$  = constant. By what amount heat is absorbed in the process in 26 °C rise in temperature? (A) 100, (B) 180, (C) 200, (D) 208, (E) 220 J.
- 4. A Carnot engine operates between 327 and 117 °C. If it absorbs 120 cal heat per cycle from the source, the heat rejected per cycle to the sink is (A) 120, (B) 42, (C) 78, (D) 90, (E) 160 cal.
- 5. AB, A<sub>2</sub>, and B<sub>2</sub> are diatomic molecules. If the bond enthalpies of A<sub>2</sub>, AB, and B<sub>2</sub> are in the ratio 2:2:1 and enthalpy of formation AB from A<sub>2</sub> and B<sub>2</sub> is -100 kJ/mol. What is the bond energy of A<sub>2</sub>? (A) 200, (B) 100, (C) 300, (D) 500, (E) 400 kJ/mol.
- 6. The reaction of zinc metal (Zn) with hydrochloric acid (HCl) was used to produce 1.5 moles of hydrogen gas (H<sub>2</sub>) at 298 K and 1 atm pressure. The magnitude work done in pushing back the atmosphere is (A) 596, (B) 634, (C) 447, (D) 298, (E) 894 cal.
- 7. In the decomposition equilibrium of a certain metallic carbonate, the partial pressure of CO<sub>2</sub> becomes a hundredfold (×100) when the temperature increased from 400 K to 500 K. What is the mean value of ΔH° for the given range of temperature? (A) 18.4, (B) 13.84, (C) 14.83, (D) 10.83, (E) 21.36 kcal/mol.
- 8. For the given chemical equation:  $2X(g) + Y(g) \rightleftharpoons 2Z(g) + 8$  kcal, which combination of pressure and temperature gives the highest yield of Z at equilibrium (A) 1000 atm and 500 °C, (B) 500 atm and 500 °C, (C) 500 atm and 100 °C, (D) 1000 atm and 100 °C, (E) 100 atm and 100 °C.
- 9. When S in the form of S<sub>8</sub> is heated at 900 K, the initial partial pressure of S<sub>8</sub> which is 1 atm falls by 30% at equilibrium. This is because of conversion of some S<sub>8</sub>(g) to S<sub>2</sub>(g). The equilibrium constant of the reaction is (A) 0.011 atm<sup>3</sup>, (B) 83.4 atm<sup>3</sup>, (C) 1.71 atm<sup>3</sup>, (D) 204.8 atm<sup>3</sup>, (E) 2.96 atm<sup>3</sup>.
- 10. Steam decomposes at high temperature according to the equation:  $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ ;  $\Delta H^{\circ} = 240$  kJ/mol and  $\Delta S^{\circ} = 50$  J/K/mol. The temperature at which the equilibrium constant becomes 1.0 is (A) 4.8, (B) 48, (C) 480, (D) 4800 K. (E) Impossible.
- 11. The rate of the reaction  $3A + 2B \rightarrow Products$  is given by the rate expression:  $r = k[A][B]^2$ . If A is taken in large excess, the reaction starts obeying (A) third-order, (B) second-order, (C) first-order, (D) zero-order kinetics. (E) None of the above.

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共 2 頁之第 2 頁

12.  $H_2O$  and O react bimolecularly to form two OH radicals.  $\Delta H$  for this reaction is 72 kJ at 500 K and activation energy  $E_a$  is 77 kJ/mol.  $E_a$  for the bimolecular recombination of two OH radicals to form  $H_2O$  and O is (A) 149, (B) 72, (C) 5, (D) 7, (E) 154 kJ/mol.

- 13. At a certain temperature and fixed volume, the rate constant for the decomposition of C<sub>2</sub>H<sub>6</sub>(g) into C<sub>2</sub>H<sub>4</sub>(g) and H<sub>2</sub>(g) is 0.0015 Pa<sup>-1</sup>h<sup>-1</sup>. If the initial pressure of C<sub>2</sub>H<sub>6</sub>(g) is 3 bar, the time for the pressure of the system to become 5 bar is (A) 0.01, (B) 0.6, (C) 6, (D) 36, (E) 120 s.
- 14. The rate equation for an autocatalytic reaction  $X + R \rightarrow R + R$  is  $r_X = k[X][R]$ . The rate of disappearance of reactant X is maximum when (A) [X] = 2[R], (B) [X] = [R], (C)  $[X] = [R]^{1/2}$ , (D)  $[X] = [R]^{1/2}$ , (E)  $[X] = [R]^{-1/2}$ .
- 15. The rate of the reaction gets doubled when the temperature changes from 7 to 17 °C. By what factor will it change for the temperature change from 17 to 27 °C? (A) 1.81, (B) 1.71, (C) 1.91, (D) 2.10, (E) 2.65.

第二部分 非選擇題(16-19),共25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。

- 16. (6%) Determine the composition of a binary mixture (A + B) for which the mixing entropy ( $\Delta S_{mix}$ ) is a maximum.
- 17. (6%) A real gas can be described by the equation  $P(V_m b) = RT$ . Derive an equation for the fugacity of this gas.
- 18. (7%) Consider the following mechanism for the overall chemical reaction  $A_2 + B \rightarrow D$ :
  - (1)  $A_2 \rightleftharpoons 2A$  (equilibrium constant  $K_1$ )
  - (2) A + B  $\rightleftharpoons$  C (equilibrium constant  $K_2$ )
  - (3)  $A_2 + C \stackrel{k}{\rightarrow} D + A$

Assuming that the equilibria are rapidly established in the first two steps, write rate expression for [D].

19. (6%) For the consecutive first-order reactions:  $A \stackrel{k_1}{\to} B \stackrel{k_2}{\to} C$ , the species B is in steady state. Derive the concentration of C as a function of time at this stage. At time t = 0,  $[A] = [A]_0$  and [B] = [C] = 0.

## 試題隨卷繳回