## 國立成功大學九十四學年度碩士班招生考試試題

編號: 4 158 系所: 化學工程學系乙組

科目:物理化學

- 1. About the first law of thermodynamics, choose the correct statement. (5%)
  - (a) The total energy of an isolated system is constant.
  - (b) The internal energy of an isolated system is constant.
  - (c) The total energy of a closed system is constant.
  - (d) Work and heat can be completely interconverted by a cyclic process.
  - (e) All above is correct.
- 2. About the second law of thermodynamics, choose the correct statement. (5%)
  - (a) The entropy of an isolated system is constant.
  - (b) Work can be completely converted into heat by any processes.
  - (c) The entropy of a system undergoing a reversible adiabatic process is increased.
  - (d) The entropy change for any cyclic process is equal to zero.
  - (e) None is correct.
- 3. For a binary liquid mixture A-B, choose the correct one. (5%)
  - (a) Both the molar volume of the solution and partial molar volume for each component are always positive.
  - (b) The molar volume of mixing is always zero.
  - (c) The Gibbs energy of the solution is always increased with increasing the temperature.
  - (d) The Gibbs energy of the solution is always increased with increasing the pressure.
  - (e) None is correct.
- 4. Choose the correct one. (5%)
  - (a) The solubility of CO<sub>2</sub> in water increases with increasing the temperature.
  - (b) The dissolution rate of CO<sub>2</sub> in water increases as the temperature is raised.
  - (c) The solubility of CO<sub>2</sub> in water increases when a salt is added.
  - (d) The dependence of dissolution rate on the temperature is determined by the heat of dissolution.
  - (e) None is correct.
- 5. Choose the correct one. (5%)
  - (a) Fuel cells offer the opportunity to achieve higher thermodynamic efficiency in the conversion of Gibbs energy to mechanical work.
  - (b) The electrical energy of a hydrogen-oxygen fuel cell is equal to the heat of combustion of hydrogen with oxygen.

(背面仍有題目,請繼續作答)

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- (c) The electrical energy of a hydrogen-oxygen fuel cell is greater than the Gibbs energy change of the corresponding reaction.
- (d) A fuel cell is a device in which the chemical energy can be completely converted into electrical energy without any energy loss.
- (e) None is correct.
- 6. The freezing of a mole of supercooled water at -10°C is an irreversible process, why? (5%)
  - (1) The entropy of water at -10°C is smaller than that of ice.
  - (2) The Gibbs energy of water at -10°C is greater than that of ice.
  - (3) The freezing of water at -10°C is an exothermic process.
  - (4) The freezing of water at -10°C is an isotropic process.

Which one is the most proper reason? (a) 1, (b) 2, (c) 3, (d) 4, (e) 1, 2 (f) 2, 3.

- 7. From the following statements, (5%)
  - (1) A gas reaction never goes to completion.
  - (2) The chemical potentials of reactants and products at reaction equilibrium are equal.
  - (3) The chemical potential of a spontaneous gas reaction is always from the higher to the lower side.
  - (4) According to Le Chatelier's principle, when an independent variable of a system at equilibrium is changed, the equilibrium shifts in the direction that tends to reduce the effect of the change.

Choose the correct one. (a) 1, 2, 4 (b) 2, 3, 4 (c) 2, 3 (d) 2, 4 (e) 1, 2, 3, 4.

- 8. An equilibrium system contains CaO(s), CO<sub>2</sub>(g), and CaCO<sub>3</sub>(s). (5%)
  - (1) The number of degree of freedom is 1.
  - (2) The number of independent reactions is 1.
  - (3) The number of phases is 2.
  - (4) The equilibrium constant is equal to the pressure of CO<sub>2</sub>.
  - (5) If the pressure of CO<sub>2</sub> is larger than the equilibrium constant, CaO(s) and CO<sub>2</sub>(g) are coexisted in the system.

Which one is correct? (a) 1, 2, 4 (b) 1, 2, 5 (c) 2, 3, 4 (d) 2, 4 (e) 1, 2, 3, 4, 5.

- 9. From the following statements, (5%)
  - (1) The vapor pressure of water is a constant at a given temperature.
  - (2) The vapor pressure of water is independent of the external pressure.
  - (3) At the curved surface of water droplet, the pressure in the outer surface

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is slightly greater than that in the inner surface.

- (4) The vapor pressure of a water droplet is slightly greater than that of water in a beaker.
- (5) Water in a small bubble has a lower vapor pressure than the bulk water because of the action of surface tension.

Choose the correct one. (a) 1, 2, 4 (b) 1, 2, 5 (c) 2, 4, 5 (d) 2, 4 (e) 1, 2, 3, 4, 5.

10. For the first-order parallel reactions (5%)

Reaction 1:  $A \xrightarrow{k_1} B$ 

$$\Delta G = -100 + 0.01T$$
 kJmol<sup>-1</sup>, k<sub>1</sub>=  $10^{13}$  exp(-500/T) s<sup>-1</sup>

Reaction 2:  $A \xrightarrow{k_2} C$ 

$$\Delta G = -1000 + T$$
 kJmol<sup>-1</sup>, k<sub>2</sub> = 10<sup>15</sup> exp(-1000/T) s<sup>-1</sup>

- (1) At 500 K, the rate of reaction 2 is faster than that of reaction 1.
- (2) At 1000 K, the species B is thermodynamically stable than C.
- (3) At room temperature, the species B is thermodynamically stable than C.
- (4) The enthalpy of reaction for reaction 1 is greater than that of reaction 2.
- (5) The entropy of reaction for reaction 1 is greater than that of reaction 2. Which one is correct? (a) 1, 4 (b) 2, 4 (c) 1, 2, 4 (d) 1, 4, 5 (e) 1, 3, 4.
- 11. One mole of steam is compressed reversibly to liquid water at the boiling point  $100^{\circ}$ C. The heat of vaporization of water at  $100^{\circ}$ C and 1.01325 bar is 2258 Jg<sup>-1</sup>. Calculate w, q,  $\Delta$ H,  $\Delta$ U,  $\Delta$ G,  $\Delta$ A, and  $\Delta$ S. (20%)
- 12. For the trimolecular reactions  $2A + M \rightarrow A_2 + M$ , the mechanism can be written

as 
$$A + M \Leftrightarrow_{k_{-1}}^{k_1} AM$$
  
 $AM + A \xrightarrow{k_2} A_2 + M$ 

- (a) Derive the steady-state rate equation. (10%)
- (b) If the intermediate is very short-lived, derive the expression of activation energy. (5%)
- (c) At which conditions the activation energy for the trimolecular reaction can be negative? (3%)
- 13. If a molecule dissociates on being adsorbed, the process is referred to as dissociative adsorption. For hydrogen molecules adsorbs on the palladium catalyst surface, derive the Langmuir adsorption isotherm for the dissociative adsorption. (12%)