編號:

103

國立成功大學九十七學年度碩士班招生考試試題

共 ユ 頁 第/頁

系所: 化學工程學系乙組

科目:物理化學

本試歷是否可以使用計算機:

☑可使用 , □不可使用

(請命題老師勾選)

考試日期:0301, 節次:3

 $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \text{x} 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} = 8.206 \text{x} 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ 

- 1. For each of the following processes, state which of the quantities  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$ , and  $\Delta G$  are equal to zero: (15%)
  - a. Isothermal reversible expansion of an ideal gas.
  - b. Adiabatic reversible expansion of a nonideal gas.
  - c. Isothermal expansion of a nonideal gas against vacuum.
  - d. Reaction between H<sub>2</sub> and O<sub>2</sub> in a thermally insulated bomb.
  - e. Reaction between H<sub>2</sub>SO<sub>4</sub> and NaOH in dilute aqueous solution at constant temperature and pressure.
- 2. The following is a set of special conditions: (12 %)
  - (a) True only for an ideal gas.
  - (b) True only for a reversible process.
  - (c) True only if S is the total entropy (system +surroundings).
  - (d) True only for an isothermal occurring at constant pressure.
  - (e) True only for an isothermal process occurring at constant volume.

Consider each of the following statements, and indicate which of the above conditions must apply in order for the statement to be true:

- a.  $\Delta H = 0$  for an isothermal process.
- b.  $\Delta S > 0$  for a spontaneous process.
- c.  $\Delta G \le 0$  for a spontaneous process.
- 3. A hydrogen-oxygen fuel cell with an acidic electrolyte is operating reversibly at a constant pressure of 1.0 bar and with unit activity of all substances. (a) Write the half-cell reactions and cell reaction, (b) calculate the maximum amount of work that could be done if 2.0 mol of hydrogen gas and 1.0 mol of oxygen gas are consumed at 298.15 K to form liquid water. (15%)

Given: For liquid water,  $\Delta_f H^o(1) = -285.83 \text{ kJ mol}^{-1}$ ,  $\Delta_f G^o(1) = -237.13 \text{k J mol}^{-1}$ .

- 4. (a) Calculate the molar entropy change when water is evaporated at its boiling point under 1 atm pressure. What are the entropy changes in (i) the system, (ii) the surroundings, (iii) the universe?
  - (b) Suppose now that the evaporated water is adiabatically compressed to half its volume and simultaneously heated to twice the absolute temperature at which it originally boiled. Assume the water vapor obeys the ideal gas law. What change of entropy of the system occurs?

Given:  $\Delta_f H^0(1) = -285.83 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^0(g) = -241.82 \text{ kJ mol}^{-1}$ ,  $C_{v,m} = 25.3 \text{ JK}^{-1}$ 

for water vapor. (15 %)

(背面仍有題目,請繼續作答)

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5. At 25.0 °C the equilibrium constant  $K_P$  for the reaction  $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$ 

is  $1.00 \times 10^{-5}$ , and  $\Delta S^{0}$  is  $41.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .

- (a) Calculate  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  at 25.0 °C. (5%)
- (b) Suppose that 1 mol of CO and 2 mol of H<sub>2</sub>O are introduced into a 10-dm<sup>3</sup> vessel at 25.0 °C. What are the amounts of CO, H<sub>2</sub>O, CO<sub>2</sub>, and H<sub>2</sub> at equilibrium? (9%)
- 6. The following data were measured for the adsorption of nitrogen on mica at 20°C:

P/atm 2.8 4.0 6.0 9.4 17.1 33.5  $v/\text{mm}^3$  (20°C and 1atm) 12.0 15.1 19.0 23.9 28.2 33.0

- (a) Draw a plot to show that the data are consistent with the Langmuir isotherm and calculate the values of  $v_m$  and K. (9%)
- (b) Suppose that 10<sup>15</sup> molecules cover 1 cm<sup>2</sup> of the surface. Make an estimate of the effective surface area of the gel. (5%)
- 7. For the gas reaction  $2N_2O_5 = 4 NO_2 + O_2$ , the mechanism can be expressed as follows:

1. 
$$N_2O_5 + M \stackrel{k_1}{\longleftrightarrow} NO_2 + NO_3 + M$$

2. 
$$NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2$$

3. 
$$NO + NO_3 \xrightarrow{k_4} 2NO_2$$

- (a) By using the steady-state method, derive the rate equation  $d[N_2O_5]/dt$  to show that the reaction is first-order with respect to  $N_2O_5$ . (9%)
- (b) If the rate law at certain temperature and pressure is expressed as

$$\frac{d[O_2]}{dt} = (1.5 \times 10^{-4} \, s^{-1})[N_2 O_5] \tag{6\%}$$

What is the half-life of the reaction under this condition?