

系所組別：化學工程學系乙組

考試科目：物理化學

考試日期：0223，節次：3

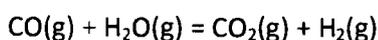
※ 考生請注意：本試題可使用計算機

1. For one mole of a van der Waals gas, $(P + \frac{a}{V_m^2})(V_m - b) = RT$, at temperature T is expanded reversibly and isothermally from a volume V_1 to a volume V_2 . (a) Show that the reversible work is $w_{rev} = -RT \ln \frac{V_2 - b}{V_1 - b} + a(\frac{1}{V_1} - \frac{1}{V_2})$, and the internal energy change is $\Delta U_m = a(\frac{1}{V_1} - \frac{1}{V_2})$. (10%) (b) If the gas expands isothermally into an evacuated vessel so that the volume changes from V_1 to V_2 , calculate w , q , and ΔU_m . (5%)

2. One mole of supercooled water at -15°C and 1 atm pressure turns into ice. Calculate the entropy change in the system and in the surroundings and the total entropy change. (13%)

Given: $C_p(\text{water}) = 75.3 \text{ JK}^{-1}\text{mol}^{-1}$, $C_p(\text{ice}) = 37.7 \text{ JK}^{-1}\text{mol}^{-1}$, $\Delta_{fus}H^\circ = 6.02 \text{ kJ mol}^{-1}$.

3. At 25.0°C the equilibrium constant K_p for the reaction (15%)



is 1.00×10^{-5} , and ΔS° is $41.8 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (a) Calculate ΔG° and ΔH° at 25.0°C .
 (b) Suppose that 1 mol of CO and 2 mol of H_2O are introduced into a 10-dm^3 vessel at 25.0°C . What are the moles of CO, H_2O , CO_2 , and H_2 at equilibrium?
 (c) What would be the effect on the equilibrium of adding N_2 to the reaction mixture in a closed stainless steel vessel?
 (d) What would be the shift of equilibrium when the temperature is increased?

4. 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/mm^3 (20°C and 1 atm)	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) Calculate the effective surface area of mica if each nitrogen molecule occupies $16.2 \times 10^{-20} \text{ m}^2$. (6%)

(背面仍有題目,請繼續作答)

Given: Langmuir isotherm is expressed as $\frac{v}{v_m} = \frac{KP}{1 + KP}$, in which v_m and K are parameters of the equation. The symbol, v_m , represents the volume of nitrogen required to form a monolayer on mica.

5. For the first-order parallel reactions (15%)



$$\Delta G = -100 + 0.01T \text{ kJ mol}^{-1}, k_1 = 10^{13} \exp(-500/T) \text{ s}^{-1}$$

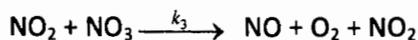
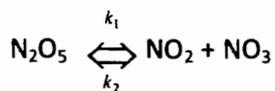


$$\Delta G = -1000 + T \text{ kJ mol}^{-1}, k_2 = 10^{15} \exp(-1000/T) \text{ s}^{-1}$$

- (a) At 500 K, is the rate of reaction 2 faster than that of reaction 1 ?
- (b) At 1000 K, is the species B thermodynamically stable than C ?
- (c) At room temperature, is the species B thermodynamically stable than C ?
- (d) Calculate the entropy changes for reactions 1 and 2, respectively.
- (e) What is the value of selectivity (defined as the rate ratio of B to C) at 1000 K ?

6. Ethanol and methanol form very nearly ideal solutions. At 20°C, the vapor pressure of ethanol is 5.93 kPa, and that of methanol is 11.83 kPa. (a) Calculate the Gibbs energy change when mixing 1 mole of methanol and 2 moles of ethanol into a solution. (b) Calculate the partial pressures and the total vapor pressure of the solution. (c) Calculate the mole fraction of methanol in the vapor. (12%)

7. The mechanism for the reaction $2\text{N}_2\text{O}_5 = 4\text{NO}_2 + \text{O}_2$ is



- (a) Derive the rate law using the steady-state approximation to show that the reaction is first-order with respect to N_2O_5 . (10%)
- (b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} , and E_{a3} for the three steps. (5%)