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(water) = 75.3 $JK^{-1}mol^{-1}$, C_P(ice)= 37.7 $JK^{-1}mol^{-1}$, $\Delta_{fus}H^o$ = 6.02 kJ mol^{-1}.

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

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$

is 1.00 x 10^{-5}, and ΔS^o is 41.8 J K^{-1} mol^{-1}.

(a) Calculate ΔG^o and ΔH^o 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 x 10^{-20} 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%)

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

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

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

$\Delta G = -1000 + T$ kJ mol^{-1}, $k_2 = 10^{15} \exp(-1000/T)$ 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 $2N_2O_5 = 4\ NO_2 + O_2$ is

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

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

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

(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 $k_3 << k_2$, 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%)