

※ 考生請注意：本試題可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

$$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1} = 8.315 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$$

1. Answer the following questions with Y (Yes) or N (No). (14 %)

- (a) $\oint dU = 0$ is always right for any process.
- (b) $\oint dq/T = 0$ is always right for any process.
- (c) Work can be obtained by an ideal gas when it is heated. The work through a constant pressure process is larger than that through a constant volume process.
- (d) For an electrolyte, the thickness of ion atmosphere is increased with increasing the ionic strength.
- (e) A gas phase reaction never goes to completion.
- (f) As the system temperature is raised, the Gibbs energy of system must be decreased.
- (g) The heat of adsorption is always negative, and the entropy of adsorption is also negative.

2. Initially at 300 K and 10 bar pressure, 1 mole of a monatomic ideal gas is allowed to expand isothermally until the final pressure reaches to 1 bar. (a) If the expansion is reversible, calculate q , w , ΔU , ΔH , ΔG , ΔA and ΔS of the system. (8 %) (b) If the expansion is free, calculate q , w , ΔU , ΔH , ΔG , ΔA and ΔS of the system. (8 %)

3. A gas flowing in a thermally insulated tube at a higher pressure is expanded through a porous plug to a lower pressure.

(a) Show that the expansion process is isenthalpic. (5 %)

(b) The Joule-Thomson coefficient μ is defined as $\mu = \left(\frac{\partial T}{\partial P}\right)_H$, show that

$$\mu = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad (6 \%)$$

(c) What is the value of μ for an ideal gas? (3 %)

4. The following thermodynamic data apply to the complete oxidation of hydrogen at 25 °C.



$$\Delta S^\circ = -163.343 \text{ J K}^{-1} \text{ mol}^{-1}$$

Suppose that a completely efficient fuel cell could be set up utilizing this reaction. (a) Calculate the maximum electrical work, and the standard emf of the cell. (8 %) (b) Calculate the maximum work that can be done with a heat engine operating reversibly between 500 °C and 25 °C if 1.0 mole of hydrogen gas and 0.5 mole of oxygen gas are reacted. Assume that all of the enthalpy change is transferred to the engine. (6 %)

5. Assume the following mechanism for a unimolecular gas reaction



- (a) Apply the steady-state assumption to A^* and obtain the rate expression $d[A]/dt$. (7%)
 (b) Show that the mechanism predicts first-order kinetic at higher A concentrations. Express the activation energy E_a in terms of E_{a1} , E_{a-1} , E_{a2} . (7%)

6. The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is



The rate equation is expressed as

$$v = k[H_2O_2][H^+][Br^-]$$

- (a) If the concentration of H_2O_2 is increased by a factor of 2, by what factor is the rate of consumption of Br^- ions increased? (3%)
 (b) If the rate of consumption of Br^- ions is $3.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, what is the rate of consumption of hydrogen peroxide? What is the rate of formation of bromine? (6%)
 (c) If the addition of water to the reaction mixture the total volume were doubled, what would be the effect of on the rate of change of the concentration of Br^- ? What would be the effect on the rate constant k ? (5%)

7. The dissociation pressures of $CaCO_{3(s)}$ versus temperature are shown as the following figure.

- (a) Which phases are there in the regions I, II, and III, respectively? (6%)
 (b) How many degrees of freedom are there when only $CaCO_{3(s)}$ and $CO_{2(g)}$ are present? (2%)
 (c) Estimate ΔG° , ΔH° and ΔS° for this equilibrium dissociation reaction at 1000 K. (6%)

Given: $P^\circ = 1 \text{ bar}$.

