

系所組別 化學工程學系乙組

考試科目 物理化學

考試日期：0307 節次 3

※ 考生請注意 本試題 可 不可 使用計算機

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

- (a) A Joule-Thomson expansion is an isenthalpic process.
- (b) The internal energy of an isolated system is constant whether it undergoes a reversible or an irreversible process.
- (c) For an irreversible process at constant temperature and pressure, the decrease in Gibbs energy is larger than the non- PV work done by the system.
- (d) The entropy is conservative for any cyclic process.
- (e) The dissolution of sodium chloride in water always causes a decrease in entropy.
- (f) The absolute zero is unattainable.
- (g) Mixing of one mole of an ideal gas at 1 bar and 300 K with two mole of the same gas at 1 bar and 300 K is a spontaneous process.

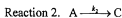
2. Considering one mole of supercooled water vapor at 95°C and 1.013 bar, choose the correct statements. (5%)

- (1) The water vapor will be spontaneously condensed into liquid water.
- (2) The water vapor can be in equilibrium with the liquid water.
- (3) The entropy of liquid water at 95°C is greater than that of water vapor.
- (4) The Gibbs energy of liquid water at 95°C is smaller than that of water vapor.
- (5) The condensation of water vapor at 95°C is an exothermic process.

3 Considering the following first-order parallel reactions, choose the correct statements. (5%)

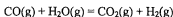


$$\Delta G = 150 - T \text{ kJ mol}^{-1}, \quad k_1 = 10^{13} \exp(-1000/T) \text{ s}^{-1}$$



$$\Delta G = 50 - 0.5T \text{ kJ mol}^{-1}, \quad k_2 = 10^{15} \exp(-5000/T) \text{ s}^{-1}$$

- (1) At 500 K, the rate of reaction 2 is faster than that of reaction 1
- (2) At 1000 K, the species B is more 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.

4. To produce more hydrogen from "synthesis gas" ($\text{CO} + \text{H}_2$) the water gas shift reaction is used.

- (a) Calculate K at 1000 K and the equilibrium extent of reaction starting with an equimolar mixture of CO and H_2O . (b) What percentage would be H_2 if the total pressure were 2.0 bar? (c) What would be the effect on the equilibrium of adding N_2 to the reaction mixture

(背面仍有題目,請繼續作答)

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※ 考生請注意：本試題 可 不可 使用計算機in a closed stainless steel vessel? (d) What would be the K value at 1200 K? (16%)

Given: At 1000 K,	species	$\Delta_f H^\circ$ (kJ mol ⁻¹)	$\Delta_f G^\circ$ (kJ mol ⁻¹)
	CO(g)	-111.983	-200.275
	H ₂ O(g)	-247.857	-192.590
	CO ₂ (g)	-394.623	-395.886

5 (a) Two moles of a monatomic ideal gas is expanded isothermally and reversibly at 30 °C from 10 to 1 bar. Calculate q , w , ΔH , ΔU , ΔG , ΔA , and ΔS for the gas.

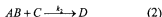
(b) If the gas is expanded into an evacuated vessel such that the final conditions are the same as in (a), calculate q , w , ΔH , ΔU , ΔG , ΔA , and ΔS for the gas. (15%)

6. (a) When one mole of hydrogen is oxidized completely to water at 25°C, how much electrical energy can be produced using a fuel cell, assuming that there are no electrical losses? What is the electromotive force of the fuel cell?

(b) When one mole of hydrogen is oxidized completely in a Carnot engine that operates between 500 and 300 K, how much electrical energy can be produced, assuming that the mechanical energy can be converted completely to electrical energy? (15%)

Given: For H₂O(l) at 25°C, $\Delta_f H^\circ = -285.83$ kJ mol⁻¹, $\Delta_f G^\circ = -237.13$ kJ mol⁻¹

7 A reaction $A + B + C \rightarrow D$ follows the mechanism



in which the first step remains essentially in equilibrium. (a) Derive the rate law for the production of D , (b) Show that the dependence of the overall rate constant k on temperature is given by

$$k = A e^{-\frac{(E_a + \Delta H)}{RT}}$$

where ΔH is the enthalpy change for the first reaction, and E_a is the activation energy for the second reaction. (15%)

8. For a van der Waals gas, $(P + \frac{a}{V^2})(\bar{V} - b) = RT$ Show that (15%)

(a) $Z = 1 + (b - \frac{a}{RT}) \frac{P}{RT}$, in which Z represents the compressibility factor.

(b) $(\frac{\partial \bar{U}}{\partial \bar{V}})_T = \frac{a}{\bar{V}^2}$