參考用

科目：物理化學(1004)　　校系所組：中央大學化學學系
交通大學應用化學系（甲組）
清華大學化學系
清華大學材料科學工程學系（丙組）

1. (20 %, 5 points for each)

(1-1) Express the definition of the Gibbs free energy.

(1-2) Under what condition, an endothermic reaction can proceed spontaneously?

(1-3) Under what condition, an exothermic reaction cannot proceed spontaneously?

(1-4) What are the second and third laws of thermodynamic?

2. (10 %, 5 points for each)

A sample of potassium ($K_{(s)}$, atomic weight = 23) of mass 2.140 g undergoes combustion in a constant-volume calorimeter with a calorimeter constant 1849 J · K^{-1} at room temperature. After the reaction completes, the temperature of the calorimeter and the inner water bath that contains 1450 g of water increases by 2.62 K. (1 cal = 4.184 J)

(2-1) Calculate ΔU_f^0 for K_2O.

(2-2) Calculate ΔH_f^0 for K_2O.

3. (20 %, 5 points for each)

Consider a reaction: 2**A** → 3**B**. Given that the standard molar enthalpies of the reactant at T_1 (=273 K) and T_2 (=373 K) are -65 kJ · mol^{-1} and 435 kJ · mol^{-1}, respectively. Also, the standard molar enthalpy of the product at T_1 and its molar heat capacity are -110 kJ · mol^{-1} and 22 kJ · K^{-1} · mol^{-1}, respectively. Assume that the enthalpies vary linearly with temperature.

(3-1) Calculate the molar heat capacity of the reactant.

(3-2) Calculate the total enthalpy of the product at T_2.

(3-3) Derive and determine if the reaction at T_1 and T_2 is endothermic or exothermic.

(3-4) Sketch in a plot showing how the total enthalpy of the reactants (2A) and that of the products (3B) vary with temperature.

注意：背面有試題

4. (26 %)

The state of an electron in a hydrogen atom is specified by three quantum numbers n, l, and m as

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

where $R_{nl}(r)$ and $Y_{lm}(\theta,\phi)$ are the radial and angular parts, respectively. Its energy is

$$E_n = \frac{hcR_H}{n^2}$$

where h is Planck's constant, c is the speed of light, and R_H is the Rydberg constant for hydrogen ($R_H = 1.097 \times 10^5\ cm^{-1}$).

(4-1) What is the quantum number n called? (4 points)

(4-2) What is the degeneracy of the $n = 2$ level? (4 points)

(4-3) For $l = 0$, 1, and 2, the corresponding subshells are denoted as s, p, and d, respectively. Which of the following transition(s) is not observed, in principle, in emission spectra? (6 points)

A) 5p → 1s　B) 4d → 3s　C) 4s → 2p　D) 5p → 3d　E) 3s → 4p

(4-4) Determine the longest possible wavelength and the shortest possible wavelength (the series limit) for lines in the Balmer series (series where the final state is the $n = 2$ level) of the spectrum of atomic hydrogen. Give your answer in units of nm. (12 points)

5. (24 %)

Consider a system of N distinguishable particles having only two energy levels 0 and ε ($\varepsilon > 0$). Suppose this system is in thermal equilibrium at temperature T.

(5-1) Find the canonical partition function Q. Use the Boltzmann constant k. (8 points)

(5-2) Find the internal energy U of the system. (8 points)

(5-3) Find the isochoric heat capacity C_V of the system. (8 points)