

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  $1849 \text{ J} \cdot \text{K}^{-1}$  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  $\Delta U_f^\circ$  for  $K_2O$ .  
(2-2) Calculate  $\Delta H_f^\circ$  for  $K_2O$ .

**3. (20 %, 5 points for each)**

Consider a reaction:  $2A \rightarrow 3B$ . Given that the standard molar enthalpies of the reactant at  $T_1$  (=273 K) and  $T_2$  (=373 K) are  $-65 \text{ kJ} \cdot \text{mol}^{-1}$  and  $435 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. Also, the standard molar enthalpy of the product at  $T_1$  and its molar heat capacity are  $-110 \text{ kJ} \cdot \text{mol}^{-1}$  and  $22 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , 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.

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## 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 ( $R_H = 1.097 \times 10^5 \text{ cm}^{-1}$ ).

(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)  $5p \rightarrow 1s$    B)  $4d \rightarrow 3s$    C)  $4s \rightarrow 2p$    D)  $5p \rightarrow 3d$    E)  $3s \rightarrow 4p$

(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  $\varepsilon$  ( $\varepsilon > 0$ ): 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)