

2017

Integrated Graduate School of Medicine, Engineering, and Agricultural Sciences, Master's Course, University of Yamanashi

## Entrance Examination

No. 1/2

Course or Program	Special Doctoral Program for Green Energy Conversion Science and Technology	Subject	Chemistry A
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## Question 1

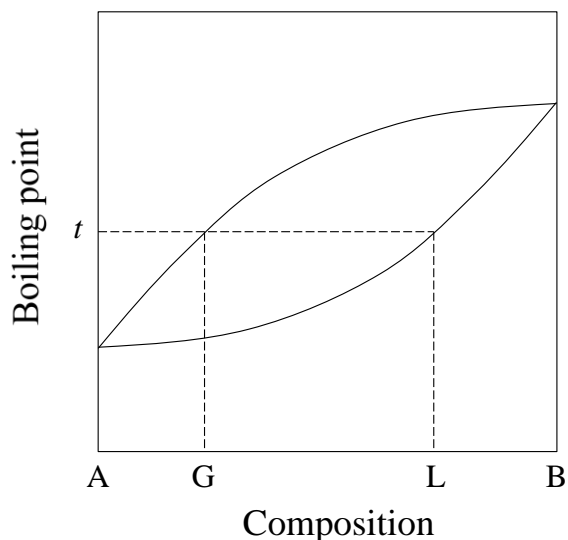
Answer the following questions. If necessary, the following value can be used: Molar gas constant,  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ .

- When 1.00 mol of benzene is boiled and vaporized at  $80^\circ\text{C}$  under 1 atm (101.3 kPa), calculate the internal-energy change when the heat of vaporization is  $30.9 \text{ kJ mol}^{-1}$ . The vapor is assumed to behave ideally.
- When 1.00 mol of an ideal gas is expanded from  $3.00 \text{ m}^3$  to  $6.00 \text{ m}^3$  in a constant-temperature process calculate the entropy change.
- When 5.00 mol of  $\text{H}_2$  and 2.00 mol of He are mixed at  $27.0^\circ\text{C}$  under 1 atm (101.3 kPa), calculate the Gibbs energy change. Both gases are supposed to behave ideally.

## Question 2

Figure on the right shows the boiling-point diagram for the composition of the gas and liquid phases containing two types of liquids. Answer the following questions.

- Suppose the composition of the boiling liquid phase is L, what is the composition of the gas phase in the equilibrium state with this boiling liquid phase.
- Write the composition of both liquid and gas phases in the equilibrium state at the boiling point,  $t$ .
- If the liquid mixture in 2) is maintained boiling, how will the boiling-point change take place?



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## Question 3

In a reaction  $A + B \rightleftharpoons C + D$ , the both of the forward and reverse reactions have a second-order rate law. The relaxation time  $\tau$  that the concentration reaches to  $1/e$  of the initial concentration is derived by a temperature jump (rapid temperature change) according to the following questions. Answer the following questions, where the concentrations of A, B, C and D are  $[A]$ ,  $[B]$ ,  $[C]$  and  $[D]$ , respectively.

- (1) When the reaction temperature increases from  $T_1$  to  $T_2$ , the rate constants of the forward and reverse reactions at  $T_2$  is  $k$  and  $k'$ , respectively. Write the reaction rate equations in the forward and reverse reactions and the net product rate  $d[A]/dt$  of A.
- (2) The concentrations of A, B, C and D in the equilibrium at  $T_2$  are  $[A]_{eq}$ ,  $[B]_{eq}$ ,  $[C]_{eq}$  and  $[D]_{eq}$ , respectively. Derive the equilibrium condition.
- (3) At the temperature  $T_2$ ,  $[A] = [A]_{eq} + x$ , where  $x$  is the deviation from  $[A]_{eq}$ . Also  $d[A]/dt = dx/dt$  is derived from this equation. Derive  $dx/dt$  from the equations derived at the questions (1) and (2).
- (4) Derive  $1/\tau$  from the equations derived at the above questions.

## Question 4

Answer the following questions about electron configurations in molecular  $B_2$  and molecular  $C_2$ .

- (1) Write the electron configuration of molecular  $B_2$ . (Ex.  $H_2$ :  $1\sigma^2$ )
- (2) Write the electron configuration of molecular  $C_2$ . (Ex.  $H_2$ :  $1\sigma^2$ )
- (3) Which does  $B_2$  or  $C_2$  have the greater bond dissociation enthalpy? Describe the reason on the basis of the bond orders of molecular  $B_2$  and molecular  $C_2$ .

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## Question 1

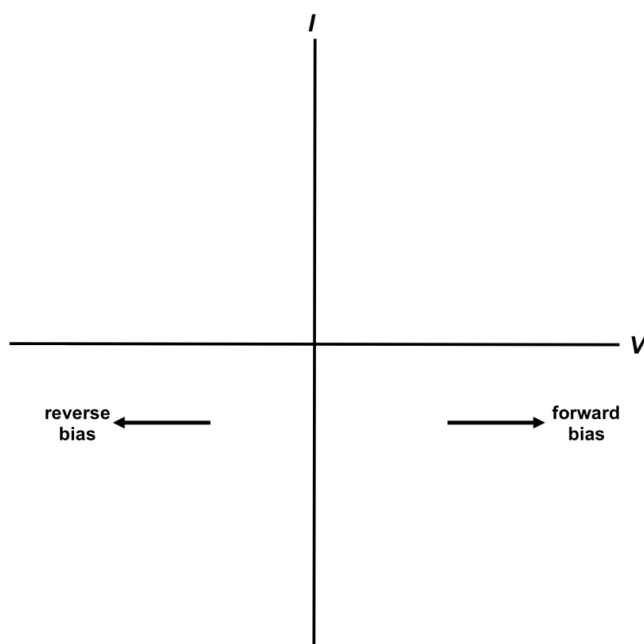
The “ $\alpha$ ” atoms (atomic radius: 120 pm) are in a cubic close-packing (ccp) array. Answer the following questions.

- (1) Draw single view drawing of the ccp array.
- (2) Calculate the maximum atomic radius of the atom that would just fit into an octahedral interstice (octahedral gap).
- (3) Calculate the maximum atomic radius of the atom that would just fit into a tetrahedral interstice (tetrahedral gap).
- (4) Answer the number of octahedral interstice and tetrahedral interstice in the ccp array composed of  $n$  pieces of the “ $\alpha$ ” atoms.

## Question 2

Answer the following questions related to an impurity semiconductor.

- (1) Draw band structure of the p-type semiconductor, and enter the acceptor level ( $E_A$ ), the Fermi level ( $E_F$ ), and the band gap ( $E_g$ ) in the band structure.
- (2) Draw band structure of the n-type semiconductor, and enter the donor level ( $E_D$ ) and the Fermi level ( $E_F$ ), and the band gap ( $E_g$ ) in the band structure.
- (3) Draw band structure of the pn-junction semiconductor, and enter the acceptor level ( $E_A$ ), the donor level ( $E_D$ ), and the Fermi level ( $E_F$ ) in the band structure.
- (4) Draw current ( $I$ ) – voltage ( $V$ ) characteristic for the pn-junction semiconductor, referring to the following figure.



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## Question 3

In all cases, the temperature is 298 K. If necessary, use the values of gas constant  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$  and Faraday constant  $F = 96500 \text{ C mol}^{-1}$ .

Answer the following questions.

(1) Explain the difference between strong and weak electrolytes in terms of concentration dependence of molar conductivity using a figure illustration. In addition, explain the determination method of molar conductivity of  $\text{NH}_4\text{OH}$  solution at infinite dilution.

(2) Calculate the ionic strength of 0.005 M  $\text{ZnCl}_2$  solution and determine the mean activity coefficient of the solution from Debye-Hückel limiting law using the constant  $A = 0.509$ .

(3) A galvanic cell using the reaction  $\text{AgCl(s)} + 1/2\text{H}_2\text{(g)} \rightarrow \text{Ag(s)} + \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$  was assembled. The standard electrode potential of  $\text{Ag} | \text{AgCl} | \text{Cl}^-$  is 0.222 V.

(a) Write the reactions of cathode and anode, and calculate the standard electromotive force.

(b) Calculate the standard Gibbs free energy of the cell reaction and state whether the reaction is spontaneous.

(c) Write the Nernst equation for the electromotive force of the cell as a function of mean activity coefficient,  $\gamma_{\pm}$ , and concentration,  $c$ , of HCl solution. Calculate the electromotive force of the cell when  $c = 0.2 \text{ mol kg}^{-1}$ ,  $\gamma_{\pm} = 0.767$  and the pressure of  $\text{H}_2\text{(g)}$  is 1 atm (101.3 kPa).