

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

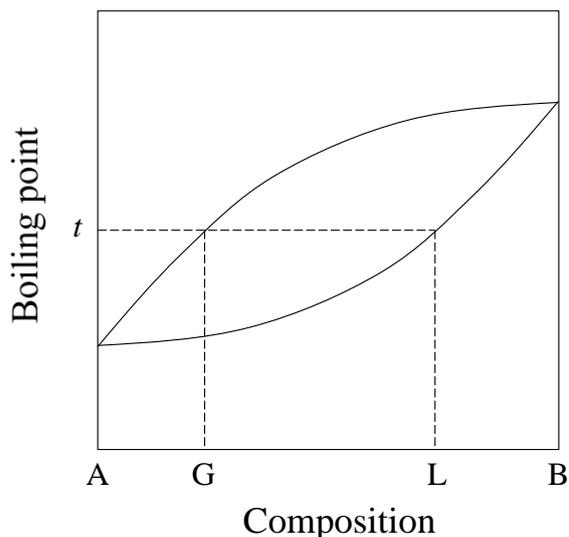
Answer the following questions. If necessary, the following value can be used: Molar gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

- When 1.00 mol of benzene is boiled and vaporized at 80°C under 1 atm (101.3 kPa), calculate the internal-energy change when the heat of vaporization is 30.9 kJ mol^{-1} . The vapor is assumed to behave ideally.
- When 1.00 mol of an ideal gas is expanded from 3.00 m^3 to 6.00 m^3 in a constant-temperature process calculate the entropy change.
- When 5.00 mol of H_2 and 2.00 mol of He are mixed at 27.0°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 τ 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

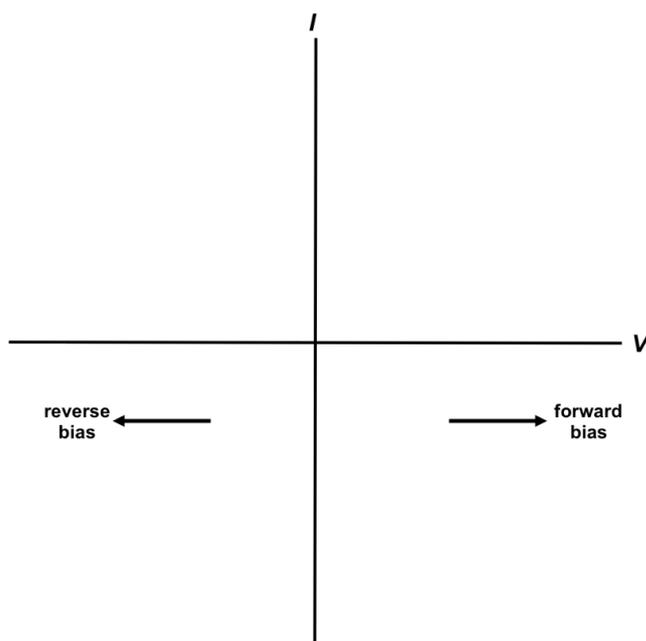
The “ α ” atoms (atomic radius: 120 pm) are in a cubic close-packing (ccp) array. Answer the following questions.

- (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 “ α ” 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 NH_4OH solution at infinite dilution.
- (2) Calculate the ionic strength of 0.005 M 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, γ_{\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).