

Question 1 (26 points). ※ 注意：請於試卷內之「選擇題作答區」依序作答。

(1). The amount of heat necessary to raise a body one degree of temperature (K or °C) is called: (a) one calorie (b) the specific heat capacity (c) the heat capacity (d) the molar heat capacity.

(2). Which of the following volumes is closest to that occupied by one mole of an ideal gas at room temperature? (a) 22.4 liters (b) 24.4 liters (c) 18.9 liters (d) 1 liter.

(3). During an adiabatic free expansion of a gas:

I. The temperature remains constant.

II. The entropy of the gas increases.

III. The internal energy of the gas remains constant

(a) I (b) I and III (c) II and III (d) I, II, and III.

(4). Using the key below, which of the following sequences represents the Carnot cycle?

AA. adiabatic expansion

BB. adiabatic compression

CC. isothermal expansion

DD. isothermal compression

(a) DD, AA, CC, BB (b) CC, AA, DD, BB (c) BB, DD, AA, CC (d) more than one of the above.

(5). Chemical equilibrium occurs when:

I. The rate of the forward reaction equals the rate of the back reaction

II. The concentrations of products and reactants attain steady state values.

III. Energy in the system is distributed in the most probably manner.

(a) I (b) I and III (c) II and III (d) I, II, and III.

(6). Which of the following statements about the relationship between G_0 , the standard free energy change, and K , the thermodynamic equilibrium constant, is untrue? (a) When ΔG_0 is large and positive, K is very small.

(b) When ΔG_0 is large and negative, K is very large. (c) When ΔG_0 is zero, $K = 1$. (d) All of the above are true.

(7). Chemical potential can be defined as $\mu_i = (\partial A / \partial n_i)_{T, V, n_j} = (\partial G / \partial n_i)_{T, P, n_j} = (\partial U / \partial n_i)_{S, V, n_j} = (\partial H / \partial n_i)_{S, P, n_j}$. Thus (a) $\Delta A_{T, V} = \sum n_i \mu_i$ (b) $\Delta G_{T, P} = \sum n_i \mu_i$ (c) $\Delta U_{S, V} = \sum n_i \mu_i$ (d) $\Delta H_{S, P} = \sum n_i \mu_i$ (e) all of the above are true.

(8). In the phase diagram of a mixture, the temperature below which a mixture is miscible in all proportions is called (a) upper critical solution temperature (b) lower critical solution temperature (c) azeotrope (d) triple point.

(9). For a two-component system, the maximum number of phases that can coexist in equilibrium is (a) 0 (b) 1 (c) 2 (d) 3.

(10). For an irreversible, isothermal, isobaric process in a closed system (a) ΔA must be negative (b) ΔG must be negative (c) ΔH must be negative (d) ΔU must be negative (e) impossible to determine from given information.

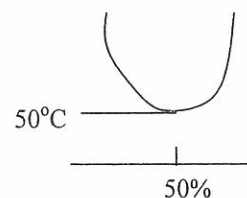
(11). If the partial pressure P_1 increases in an ideal gas mixture held at constant T , then μ_1 in the mixture (a) increases (b) decreases (c) remains the same (d) impossible to determine from given information.

(12). For an ideal gas, entropy is a function of (a) temperature only (b) temperature and pressure (c) pressure only (d) none of the above.

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(13). A phase diagram is shown on the right. Which of the following is wrong?

- (a) A critical solution temperature exists.
- (b) As temperature increases, the mutual solubility of A and B increases.
- (c) At 40°C, we have a single phase solution.
- (d) There may be strong associating interactions such as strong polar interactions or hydrogen bonds existing within the systems.



Question 2 (36points). ※ 注意：請於試卷內之「選擇題作答區」依序作答。

(14). Based on the Debye-Hückel limiting law, estimate the mean ionic activity coefficient of a solution that is $0.02 \text{ kgmol}^{-1} \text{ CaCl}_{2(aq)}$ and $0.03 \text{ kgmol}^{-1} \text{ NaF}_{(aq)}$ at 25°C. (a) = 0.45, (b) = 0.56, (c) = 0.66, (d) = 0.71, or

(e) 0.82.

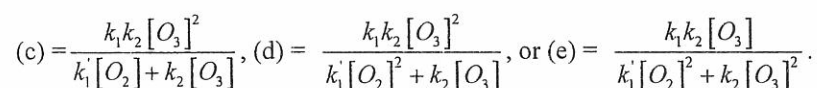
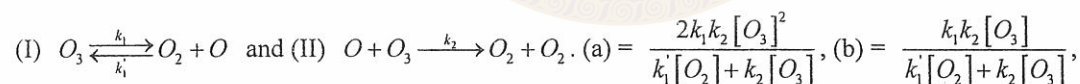
(15). For a half cell reaction, $1/2 \text{ H}_{2(g)} = \text{H}_{(aq)}^+ + e^-$. What is the standard molar entropy of an electron, $\bar{S}^0(e^-)$?

(a) = $\bar{S}^0(\text{H}_{(aq)}^+)$, (b) = $\bar{S}^0(\text{H}_{(aq)}^+)/2$, (c) = $\bar{S}^0(\text{H}_{2(g)})$, (d) = $\bar{S}^0(\text{H}_{2(g)})/2$, or (e) = 0.

(16). The diffusion coefficient of CCl_4 in heptane at 25°C is $3.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Estimate the time required for a CCl_4 molecule to have a root mean square displacement of 5.0mm. (a) = 1300, (b) = 1950 (c) = 3900, (d) 1150, or (e) 965 seconds.

(17). At 400K, the half-life for the decomposition of a sample of a gaseous compound initially at 363 Torr was 410s. When the pressure was 169 Torr, the half-life was 880s. Determine the order of the reaction. (a) = 3, (b) = 2.5, (c) = 2, (d) = 1.5, or (e) = 1.

(18) Derive the rate law for the decomposition of ozone in the reaction $2\text{O}_{3(g)} \rightarrow 3\text{O}_{2(g)}$ on the basis of the following proposed mechanisms of (I) and (II):



(19). A typical diffusion coefficient for small molecules in aqueous solution at 25°C is $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. If the critical reaction distance is 0.4nm, what value is expected for the second-order rate constant for a diffusion-controlled reaction. (a) = 4×10^9 , (b) = 8×10^9 , (c) = 1.5×10^{10} , (d) = 3×10^{10} , or (e) = $6 \times 10^{10} \text{ Lmol}^{-1}\text{s}^{-1}$

(20). The enzyme-catalyzed conversion of a substrate at 25°C has a Michaelis constant of 0.035 molL^{-1} . The rate of the reaction is $1.15 \times 10^{-3} \text{ molL}^{-1}\text{s}^{-1}$ when the substrate concentration is 0.11 molL^{-1} . What is the maximum velocity of this enzymolysis? (a) = 9.72×10^{-3} , (b) = 8.16×10^{-3} , (c) = 6.35×10^{-3} , (d) = 3.79×10^{-3} , or (e) = $1.52 \times 10^{-3} \text{ Lmol}^{-1}\text{s}^{-1}$.

(21). The absorption of a gas is described by the Langmuir isotherm with a Langmuir constant $K = 0.85 \text{ kPa}^{-1}$ at 25°C. Calculate the pressure at which the fractional surface coverage is 0.15. (a) = 0.17, (b) = 0.18, (c) = 0.19, (d) = 0.20, or (e) 0.21 kPa.

(22). The limiting molar conductivities of KCl , KNO_3 , and $AgNO_3$ are 14.99, 14.5, and 13.34 $mS\ m^2\ mol^{-1}$, respectively (all at 25°C). What is the limiting molar conductivity of $AgCl$ at this temperature? (a) = 14.28, (b) = 13.83, (c) = 13.56, (d) = 12.85, or (e) = 12.14 $mS\ m^2\ mol^{-1}$.

Question 3 (24 points)

For a two-component system (ethanol(1)-toluene(2)), the experimental vapor-liquid results are as follows:

$$T = 45^\circ C \quad P = 183\ mmHg$$

$$x_1 = 0.3 \quad y_1 = 0.634$$

The saturated vapor pressures of ethanol and toluene at 45°C are

$$p_1^{sat} = 173(\ mmHg) \quad p_2^{sat} = 75.4(\ mmHg).$$

Please answer the following questions: ※ 本大題請於試卷內之「非選擇題作答區」標明題號依序作答。

- (3.1). What are the liquid phase activity coefficients of components 1 and 2, γ_1 and γ_2 ?
- (3.2). What is the excess Gibbs free energy of the liquid phase, G^E/RT ?
- (3.3). What is the Gibbs free energy of the liquid phase, $\Delta G/RT$? Explain the reason of the sign (+ or -) for $\Delta G/RT$?
- (3.4). Does the solution have a positive or negative deviation from ideal solution?
- (3.5). If we know

$$\frac{\Delta H}{RT} = \frac{H^E}{RT} = 0.437$$

What is the excess Gibbs free energy of the liquid phase, G^E/RT at 60°C? Can you determine γ_1 and γ_2 at 60°C based on the value of G^E/RT at 60°C? Why?

Hint:
$$\frac{H^E}{RT} = -T \left(\frac{\partial (G^E/RT)}{\partial T} \right)_{P,x}$$

Question 4 (14 points). ※ 本大題請於試卷內之「非選擇題作答區」標明題號依序作答。

The pK_a of NH_4^+ is 9.25 at 25°C. The rate constant at 25°C for the reaction of NH_4^+ and OH^- to form aqueous NH_3 is $4.0 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$.

- (4.1). Calculate the rate constant for proton transfer to NH_3 .
- (4.2). What relaxation time would be observed if a temperature jump were applied to a solution of $0.15\ mol\ L^{-1}$ $NH_{3(aq)}$ at 25°C.

