科目:物理化學(A)

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#### 第一部分選擇題(1~28),每題3分,請務必使用試卷第一頁[選擇題作答區]作答

An ideal gas of constant heat capacity (30 J/mol K) undergoes reversible isothermal expansion from 1 m<sup>3</sup>/mol to 10 m<sup>3</sup>/mol and 300 K. Determine the property change (property in the final state – property in the initial state) of the gas during the process. For each problem, choose an answer that is closest to the exact solution.

- 1. What is the change in internal energy (kJ/mol)? (a) 9 (b) 3 (c) 0 (d) -3 (e) -9
- 2. What is the change in the entropy (J/mol K)? (a) 30 (b) 20 (c) 0 (d) -20 (e) -30
- 3. What is the amount of heat transferred to the gas (kJ/mol)? (a) 8 (b) 6 (c) 4 (d) 2 (e) 0

The denature of a protein with increasing temperature or decreasing pressure can be thought as a phase transition, as shown in the diagram below. At low temperature and high pressure, protein is more stable in the folded (active) state, whereas at high temperature and low pressure, protein becomes more stable in the extended

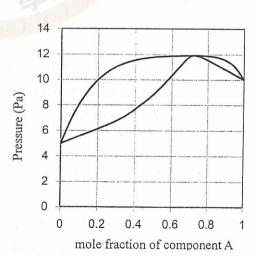
(denatured) state. Determine the property change D (property of denatured protein – property of active protein) at the transition temperature and pressure (i.e., the solid line)

- 4. What is the change in enthalpy? (a) ΔH>0 (b)
   ΔH=0 (c) ΔH<0 (d) no definite answer</li>
- 5. What is the change in entropy? (a)  $\Delta S>0$  (b)  $\Delta S=0$  (c)  $\Delta S<0$  (d) no definite answer

active protein denatured protein temperature

The vapor-liquid equilibrium diagram of a binary mixture of species A and B at 300 K is shown in the figure on the right. Choose an answer that is closest to the exact solution.

6. How would the phase change if a mixture (containing 0.3 mole fraction of A) is isothermally compressed from 2 Pa to 14 Pa at 300 K? (a) liquid → vapor (b) liquid → liquid+vapor → vapor (c) vapor→liquid (d) vapor → liquid+vapor → liquid (e) liquid → vapor → liquid



7. What is the composition (mole fraction of A) of the vapor phase that is in

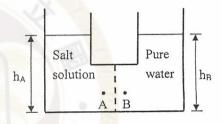
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equilibrium with a liquid containing 0.2 mole fraction of A at 10 Pa and 300 K? (a) 0.2 (b) 0.4 (c) 0.6 (d) 0.8 (e) 1.0

- 8. What is the activity coefficient of species B in the liquid mixture containing 0.2 mole fraction of A at 300 K? (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
- 9. What is the fugacity (in Pa) of species B in the liquid mixture containing 0.2 mole fraction of A at 300 K? (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
- 10. What is the fugacity (in Pa) of species B in the gas mixture containing 0.2 mole fraction of A at 300 K and 5 Pa? (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
- 11. What is the Gibbs free energy (J/mol) of mixing of the liquid mixture containing 0.2 mole fraction of A at 300 K? (a) 600 (b) 300 (c) 0 (d) -300 (e) -600

A tube is divided into two parts by a semi-permeable membrane as shown in the figure on the right. The membrane only allows the passage of water but not sodium chloride through the membrane. Suppose salt solution and pure water are poured the two ends of the tube, respectively, and the initial liquid surface level are the same (i.e., h<sub>A</sub>=h<sub>B</sub>).



- 12. What are the surface levels of the two liquid surfaces when the system reaches equilibrium? (a) h<sub>A</sub>=h<sub>B</sub> (b) h<sub>A</sub>>h<sub>B</sub> (c) h<sub>A</sub><h<sub>B</sub> (d) no definite answer
- 13. At equilibrium, what is the pressure at point A  $(P_A)$  and point B  $(P_B)$ ? (a)  $P_A = P_B$  (b)  $P_A > P_B$  (c)  $P_A < P_B$  (d) no definite answer
- 14. At equilibrium, what is the chemical potential of water at point A ( $\mu_A$ ) and point B ( $\mu_B$ )? (a)  $\mu_A = \mu_B$  (b)  $\mu_A > \mu_B$  (c)  $\mu_A < \mu_B$  (d) no definite answer
- 15. Using the Debye-Hückel limiting law, calculate the value of the activity in a  $7.5\times10^{-3}\ mol\ kg^{-1}$  solution of  $Na_2SO_4$ . (a) 0.0142, (b) 0.0125, (c) 0.0096, (d) 0.0084, or (e) 0.0073.
- 16. You are given the following half-cell reactions:

$$Pd_{(aq)}^{2+} + 2e^{-} \rightarrow Pd_{(s)}$$
  $E^{0} = 0.83V$   
 $PdCl_{4(aq)}^{2-} + 2e^{-} \rightarrow Pd_{(s)} + 4Cl_{(aq)}^{-}$   $E^{0} = 0.64V$ 

Calculate the equilibrium constant for the reaction  $Pd_{(aq)}^{2+} + 4Cl_{(aq)}^{-} \rightarrow PdCl_{4(aq)}^{2-}$ .

(a)  $2.65 \times 10^6$ , (b)  $5.83 \times 10^6$ , (c)  $8.17 \times 10^6$ , (d)  $9.84 \times 10^6$ , or (e)  $1.44 \times 10^7$ .

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17. The pressure in interplanetary space is estimated to be of the order of  $10^{-14} Pa$ . Calculate the mean free path between particles in the space. Assume that only hydrogen atoms with a collision diameter, d = 0.2nm are p resent and that the temperature is 1000K. (a)  $3.6 \times 10^{13}$ , (b)  $7.8 \times 10^{12}$ , (c)  $2.5 \times 10^{12}$ , (d)  $8.9 \times 10^{11}$  or (e)  $4.2 \times 10^{11}$  meter.

18. Estimate the effective radius of a sucrose molecule in water at 25°C given that its diffusion coefficient is  $5.2 \times 10^{-12} m^2 s^{-1}$  and that the viscosity of water is 1.00cP.

(a)  $9.8 \times 10^{-10} m$ , (b)  $6.4 \times 10^{-10} m$ , (c)  $4.2 \times 10^{-10} m$ , (d)  $2.5 \times 10^{-10} m$ , or (e)  $1.3 \times 10^{-10} m$ 

19. You are given the following data for the decomposition of acetaldehyde:

Initial concentration (M)	9.72×10 <sup>-3</sup>	4.56×10 <sup>-3</sup>	
Half-Life (s)	328	685	

Determine the rate constant for the reaction. (a)  $2.1 \times 10^{-3} s^{-1}$ , (b)  $1.0 \times 10^{-3} s^{-1}$ , (c)  $0.83 M^{-1} s^{-1}$ , (d)  $0.59 M^{-1} s^{-1}$ , or (e)  $0.32 M^{-1} s^{-1}$ .

- 20. The mobility of a chloride ion in aqueous solution at 25°C is  $7.91 \times 10^{-8} \, m^2 \, s^{-1} V^{-1}$ . Calculate the molar ionic conductivity. (a)  $7.63 \times 10^{-3} \, S \, m^2 \, mol^{-1}$ , (b)  $5.48 \times 10^{-3} \, S \, m^2 \, mol^{-1}$ , (c)  $3.62 \times 10^{-3} \, S \, m^2 \, mol^{-1}$ , (d)  $1.64 \times 10^{-3} \, S \, m^2 \, mol^{-1}$ , or (e)  $0.65 \times 10^{-3} \, S \, m^2 \, mol^{-1}$ .
- 21. The rate constant for the first-order decomposition of  $N_2O_5$  in the reaction  $2N_2O_{5(g)} \to 4NO_{2(g)} + O_{2(g)}$  is  $k = 3.38 \times 10^{-5} \, s^{-1}$  at 25 °C. What is the half-life of  $N_2O_5$ ? (a)  $5.47 \times 10^4 \, s$ , (b)  $4.61 \times 10^4 \, s$ , (c)  $3.10 \times 10^4 \, s$ , (d)  $2.06 \times 10^4 \, s$ , or (e)  $1.03 \times 10^4 \, s$
- 22. In a photochemical reaction  $A \rightarrow 2B + C$ , the quantum efficiency with 500nm

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light is  $2.1\times10^2$  mol einstein<sup>-1</sup>. After exposure of 300 mmol of A to the light, 2.28 mmol of B is formed. How many photons were absorbed by A? (a)  $7.6\times10^{18}$ , (b)  $5.8\times10^{18}$ , (c)  $3.3\times10^{18}$ , (d)  $1.6\times10^{18}$ , or (e)  $0.25\times10^{18}$ .

- 23. To use collision theory we must know the fraction of molecular collisions having at least the kinetic energy  $E_a$  along the line of flight. What is this fraction when  $E_a = 10kJmol^{-1}$  at 300K? (a) 0.18, (b) 0.018, (c) 0.0018, (d) 0.00018, or (e) 0.000018.
- 24. The forward rate constant for the elementary reaction  $C_2H_6 \rightarrow 2CH_3$  is  $1.57 \times 10^{-3} \, s^{-1}$  at  $1000 \, K$ . The Gibbs energy of formation for methyl radical  $\Delta_f G \left( CH_3 \cdot \right)$  and for ethane,  $\Delta_f G \left( C_2H_6 \right)$ , is  $159.74 \, kJ/mol$  and  $109.55 \, kJ/mol$ , respectively at  $1000 \, K$ . What is the rate constant for the backward reaction at this temperature? (a)  $5.82 \times 10^{11} \, Lmol^{-1} \, s^{-1}$ , (b)  $2.17 \times 10^{11} \, Lmol^{-1} \, s^{-1}$ , (c)  $6.58 \times 10^{10} \, Lmol^{-1} \, s^{-1}$ , (d)  $1.21 \times 10^{10} \, Lmol^{-1} \, s^{-1}$ , or (e)  $8.37 \times 10^9 \, Lmol^{-1} \, s^{-1}$ .
- 25. Consider the decomposition of  $NOCl: 2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$ . The Arrhenius activation energy for this reaction is  $E_a = 104kJmol^{-1}$ . Calculate the enthalpy of activation,  $\Delta H^{\ddagger}$ , for the reaction at 300K base d on the Eyring equation. The symbol,  $\ddagger$ , stands for the transition state of the reaction. (a)  $104.0\,kJmol^{-1}$ , (b)  $101.5\,kJmol^{-1}$ , (c)  $99.0\,kJmol^{-1}$ , (d)  $91.5\,kJmol^{-1}$ , or (e)  $89.0\,kJmol^{-1}$
- 26. Biacetyl triplets has a quantum yield of 0.25 for phosphorescence and a measured lifetime of the triplet state of  $10^{-3} s$ . If its phosphorescence is quenched by a compound Q with a diffusion-controlled rate  $(10^{10} L mol^{-1} s^{-1})$ , what concentration of Q is required to cut the phosphore scence yield by half by using the Stern-Volmer equation? (a)  $10^{-7} mol L^{-1}$ , (b)  $10^{-8} mol L^{-1}$ , (c)  $10^{-9} mol L^{-1}$ , (d)  $10^{-10} mol L^{-1}$ , or (e)  $10^{-11} mol L^{-1}$ .

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27. For a condensation polymerization of a hydroxyl acid in which 99% of the acid groups are used up, calculate the average number of monomer units in the polymer molecules. (a) 10000, (b) 1000, (c) 500, (d) 100, or (e) 10

28. The pressure of nitrogen required for adsorption of  $1.0cm^3 g^{-1}$  of gas on graphitized carbon black are 24Pa at 77.5K and 290Pa at 90.1K. Calculate the enthalpy of adsorption at this fraction of surface coverage. (a)  $-20.3kJmol^{-1}$ , (b)  $-18.4kJmol^{-1}$ , (c)  $-15.6kJmol^{-1}$ , (d)  $-13.8kJmol^{-1}$ , or (e)  $-11.6kJmol^{-1}$ .

第二部分計算題(29~30),每題8分

- 29. Determine the maximum work (kJ/mol) that can be obtained from mixing two equal molar fluids under constant pressure of 5 bar and constant temperature of 300 K if the two fluids are (8 points)
  - (a) two pure ideal gases
  - (b) two pure liquids and the excess Gibbs free energy of the mixture can be described by  $\underline{G}^{ex}(J/mol) = 10 x_1 x_2 RT$ , where R is the ideal gas constant, T is temperature,  $x_1$  and  $x_2$  are the mole fractions of the two fluids, respectively.
- 30. Determine the predicted rate law expression of the product, *P*, for the following radical-chain reaction: (8 points)

$$A_2 \xrightarrow{k_1} 2A$$

$$A \cdot \xrightarrow{k_2} B \cdot + C$$

$$A \cdot + B \cdot \xrightarrow{k_3} P$$

$$A \cdot + P \xrightarrow{k_4} B \cdot$$

## 試題隨卷繳回