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國立臺灣大學 103 學年度碩士班招生考試試題

科目:物理化學(A)

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第一部分單選題(1~15),每題 4 分,共 60 分,※ 注意:請於試卷內之「選擇題作答區」依序作答。

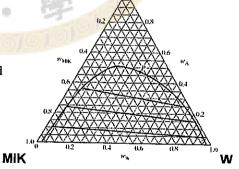
- 1. The time for 1 dm<sup>3</sup> air to effuse through an orifice is 10 minutes under a pressure of 1 bar. How long (minutes) will it take for the same volume of hydrogen gas to effuse under the same condition? (choose one that is closest to the correct answer) (a) 15 (b) 10 (c) 7.5 (d) 2.5 (e) 0.5.
- The freezing point of pure solvent A is 10 °C and its freezing point depression constant is 5 K-kg/mol. When 1 g of solid B is dissolved in 100 g of A, the freezing point of the solution drops to 9.5 °C. Which of the following values is closest to the molecular weight (in unit of g/mol) of B?
   (a) 100 (b) 80 (c) 50 (d) 32 (e) 18.

One mole of an ideal gas in a cylinder initially at 10 bar is allowed to expand against a piston that supports 2 bar. The gas and cylinder is maintained at 25 °C throughout the expansion. The constant pressure heat capacity of the gas is 30 J/mol K. In the following problems, choose a value that is closest to the correct solution.

- 3. What is the change (property in the final state property in the initial state) in the enthalpy (kJ) of the gas? (a) -100 (b) -10 (c) 0 (d) 10 (e) 100.
- 4. What is the change in entropy (J/K) of the gas? (a) -100 (b) -10 (c) 0 (d) 10 (e) 100.
- 5. How much heat (kJ) is absorbed by the gas? (a) 0 (b) 2 (c) 4 (d) 6 (e) 8.

The phase diagram for acetone(A)-water(W)-methyl isobutyl ketone (MIK) ternary mixture at 25 °C is given in the figure on the right. Note that the compositions are given in weight fractions.

6. Initially 2 g of acetone, 4 g of water, and 4 g of MIK are mixed, which of the following is closest to the concentration ratio (wt/wt) of acetone in the two equilibrium phases? (a) 1.2 (b) 1.6 (c) 2.3 (d) 3.5 (e) 4.4.



What is the minimum additional amount (g) of acetone needing to be added to the
mixture in the previous problem in order to have a single liquid phase? (a) 2 (b) 4
(c) 6 (d) 8 (e) 10.

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8. The triple point pressure of water is about 612 Pa. Estimate the entropy of vaporization (J/mol/K) of water at its normal boiling point. (a) 10<sup>2</sup> (b) 10<sup>3</sup> (c) 10<sup>4</sup> (d)  $10^6$  (e)  $5 \times 10^6$ .

- 9. The radius of the ionic atmosphere  $(1/\kappa)$  for a univalent electrolyte is 0.964 nm at a concentration of 0.10 M in water at 25 °C ( $\varepsilon$  = 78). Which of the following is closest to the radius (nm) of the ionic atmosphere in water at a concentration of 0.0001 M? (a) 0.964 (b) 1.928 (c) 60.1 (d) 30.5.
- 10. Which of the following is closest to the standard electrode potential (V) for the reaction  $Cr^{3+} + 3e^{-} \rightarrow Cr$  at 298 K? (a) -0.90 (b) -1.80 (c) -2.70 (d) -3.60.

The necessary 
$$E^o$$
 values are  
 $Cr^{3+} + 3e^- \rightarrow Cr$   $E^o = -0.74 \text{ V}$   
 $Cr^{3+} + e^- \rightarrow Cr^{2+}$   $E^o = -0.41 \text{ V}$ 

11. The enzyme glycollate oxidase is a catalyst for the reduction of cytochrome c in its oxidized form—denoted as cytochrome c (Fe<sup>3+</sup>)—by glycollate ions. The relevant standard electrode potentials E°, relating to 25 °C and pH 7, are as

reaction //	<i>E°</i> '/V
cytochrome $c$ (Fe <sup>3+</sup> ) + $e$ $\rightarrow$ cytochrome $c$ (Fe <sup>2+</sup> )	0.250
$\frac{\text{glyoxylate}^{-} + 2\text{H}^{+} + 2e^{-} \rightarrow \text{glycollate}^{-}}{\text{glycollate}^{-}}$	-0.085

Which of the following is closest to the equilibrium ratio

[cytochrome c (Fe<sup>2+</sup>)]<sup>2</sup>[glyoxylate<sup>-</sup>] at pH 7 and 25 °C? (a)  $2.1 \times 10^{11}$  (b)  $2.1 \times 10^6$  (c)  $2.1\times10^{22}$ (d) 2.1.

- 12. The isotope <sup>32</sup><sub>15</sub>P emits radiation and has a half-life of 14.3 days. What percentage of the initial activity remains after 10 days? (a) 30.6% (b) 61.6% (c) 37.9% (d) 0.78%.
- 13. The density of liquid mercury at 273 K is 13.6 g cm<sup>-3</sup> and the surface tension is 0.47 N m<sup>-1</sup>. If the contact angle is 140°, which of the following is closest to the capillary depression in a tube of 1-nm diameter? (a) -10.8 m (b) -10.8 mm (c) -10.8 cm (d) -10.8 dm.

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14. The following data apply to an enzyme-catalyzed reaction:

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	Substrate [S]/mol dm <sup>-3</sup>	Rate, v/mol dm <sup>-3</sup> s <sup>-1</sup>	
	$2.5 \times 10^{-4}$	$2.3 \times 10^{-4}$	
į	$5.0 \times 10^{-3}$	7.8 × 10 <sup>-4</sup>	

The concentration of the enzyme is 2 g dm<sup>-3</sup> and its molecular weight is 50000 g/mol. Assume the Michaelis-Menten equation to apply and calculate the Michaelis constant  $K_m$  and the limiting rate V.

- (a)  $K_m = 3.6 \times 10^{-4} \text{ (mol dm}^{-3}\text{) and } V = 9 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$
- (b)  $K_m = 3.6 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \text{ and } V = 4.5 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$
- (c)  $K_m = 7.2 \times 10^{-4}$  (mol dm<sup>-3</sup>) and  $V = 9 \times 10^{-4}$  (mol dm<sup>-3</sup> s<sup>-1</sup>)
- (d)  $K_m = 7.2 \times 10^{-4}$  (mol dm<sup>-3</sup>) and  $V = 4.5 \times 10^{-4}$  (mol dm<sup>-3</sup> s<sup>-1</sup>).
- 15. The following data relate to the adsorption of nitrogen at 77 K on a 1.00-g sample of silica gel:

P/kPa	15.2	54.8
V/cm <sup>3</sup> (STP)	135	247

At 77 K the saturation vapor pressure  $P_0$  of nitrogen is 101.3 kPa. Taking the molecular area of nitrogen to be 1.62 × 10<sup>-19</sup> m<sup>2</sup>, which of the following is closest to the specific surface area of the gel (m<sup>2</sup>/g)? (a) 1000 (b) 500 (c) 250 (d) 750.

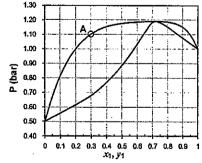
The BET equation: 
$$\frac{PP_0}{V(V_0-P)} = \frac{1}{V_0K} + \frac{P}{V_0}$$

## 第二部分計算題(16-20),共30分,每題配分註記於題號後

16. (5%) Derive the expressions for the second virial coefficient and the Boyle temperature based on the van der Waals equation of state,  $P = \frac{RT}{V-h} - \frac{a}{V^2}$ . Note that  $(1-x)^{-1} = 1 + x + x^2 + \cdots$ 

The P-x-y diagram of vapor-liquid equilibrium of a binary mixture at 300 K is shown in the figure on the right.

- 17. (5%) Determine the fugacity, fugacity coefficient, activity, activity coefficient, and partial molar excess Gibbs free energy of component 1 in the mixture at point A.
- 18. (5%) Determine the minimum work



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necessary to separate one mole of liquid mixture at point A to two pure liquids under constant temperature and pressure.

19. (8%) A substance decomposes according to first-order kinetics; the rate constants at various temperatures are as follows:

Temp (°C)	Rate constant k, (s <sup>-1</sup> )
15.0	4.18 × 10 <sup>-6</sup>
20.0	$7.62 \times 10^{-6}$
25.0	1.37 × 10 <sup>-5</sup>
30.0	$2.41 \times 10^{-5}$
37.0	$5.15 \times 10^{-5}$

Assume that the Arrhenius equation can be applied. Determine at 25 °C, the energy of activation, the Gibbs energy of activation, the enthalpy of activation, and the pre-exponential factor.

20. (7%) Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation

$$N_2O_5 + NO = 3NO_2$$

The following mechanism has been proposed.

$$N_2O_5 \rightarrow NO_2 + NO_3$$
  
 $NO_2 + NO_3 \rightarrow N_2O_5$ 

$$NO + NO_3 \rightarrow 2NO_2$$

Assume that the steady-state treatment can be applied to NO<sub>3</sub>, derive an equation for the rate of consumption of N<sub>2</sub>O<sub>5</sub>.

第三部分問答題(21~22),共10分,每題配分註記於題號後。

- 21. (4%) Describe the principle, advantages, current research challenge, etc. for any two of the following three types of electrochemical cells.
  - (a) Fuel cells
  - (b) Photogalvanic cells (or Dye-sensitized solar cells)
  - (c) Lithium ion batteries
- 22. (6%) Define (Explain) the following terms/question.
  - (a) The Carnot cycle. (b) Entropy. (c) Why is the reversible work done by a system the maximum work?

## 試題隨卷繳回