

# 大同大學 101 學年度研究所碩士班入學考試試題

考試科目：物理化學

所別：化學工程研究所

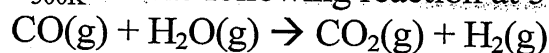
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註：本次考試 不可以參考自己的書及筆記； 不可以使用字典； 可以使用計算器。

1. (10%) (a) Plot the P-T phase diagrams for H<sub>2</sub>O and CO<sub>2</sub>. The triple point and critical point of H<sub>2</sub>O and CO<sub>2</sub> are
- |                  |                            |                               |
|------------------|----------------------------|-------------------------------|
| H <sub>2</sub> O | T <sub>tp</sub> = 0.01 °C  | P <sub>tp</sub> = 0.00611 bar |
|                  | T <sub>c,p</sub> = 374 °C  | P <sub>c,p</sub> = 215 bar    |
| CO <sub>2</sub>  | T <sub>tp</sub> = -56.4 °C | P <sub>tp</sub> = 5.11 bar    |
|                  | T <sub>c,p</sub> = 31.1 °C | P <sub>c,p</sub> = 73 bar     |
- (b) How to use the Clapeyron equation to the phase transition?

2. (10%) State briefly the zero law, the first law, the second law and the third law of the thermodynamics.

3. (15%) Determine  $\Delta H_{500K}$  for the following reaction at 500K and constant pressure:



The following data are necessary:

Substance	C <sub>p</sub> (J/mol K)	Δ <sub>f</sub> H <sub>298K</sub> (kJ/mol)
CO	29.12	-110.5
H <sub>2</sub> O	33.58	-241.8
CO <sub>2</sub>	37.11	-393.5
H <sub>2</sub>	29.89	0

4. (10%) The expansion coefficient of a gas,  $\alpha$ , is defined as  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  and the isothermal compressibility

of a gas,  $\kappa$ , is defined as  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$

(a) Find the values of  $\alpha$  and  $\kappa$  for an ideal gas at STP.

(b) Using the cyclic rule to show that  $\left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa}$

$$\left( \frac{\partial V}{\partial P} \right)_T = \frac{P}{nRT}$$

5. (15%) The following data relate to the adsorption of nitrogen at 77K on a 1.00 g sample of silica gel:

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

At 77K the saturation vapor pressure P<sub>0</sub> of nitrogen is 101.3 kPa. Estimate the surface area of the gel by BET isotherm given below by taking the molecular area of nitrogen to be 1.62x10<sup>-19</sup> m<sup>2</sup>.

$$\frac{PP_0}{V(P_0 - P)} = \frac{1}{V_0 K} + \frac{P}{V_0}$$

6. (13%) A second order reaction in solution has a rate constant of  $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C and of  $1.60 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 40 °C. Assume a proper equation to apply and calculate the activation energy and preexponential factor. What is the unit for this reaction rate?

$$k = A e^{-E_a/RT}$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

7. (15%) A homogeneous reaction of stoichiometry  $A + B \rightleftharpoons Y + Z$  is found to be second order in A and zero order in B. Please propose a mechanism and show it is consistent with this behavior.

8. (12%) Explain the meaning of following terms in Chinese.

- (a) Catalysis
- (b) Initial rate method
- (c) Adsorption isotherm
- (d) Fuel cells