

國立成功大學

113學年度碩士班招生考試試題

編 號： 77

系 所： 化學工程學系

科 目： 物理化學

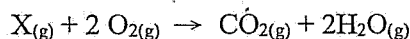
日 期： 0201

節 次： 第 3 節

備 註： 可使用計算機

※ 考生請注意：本試題可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. [15%] A gaseous hydrocarbon X at 25 °C was burned with oxygen to form CO₂ and H₂O:



- (a) Derive the adiabatic flame temperature of system burned at constant volume in the amount of oxygen required to give complete combustion forming CO₂ and H₂O. [5%]
- (b) What is the flame temperature of this system under constant pressure conditions? [5%]
- (c) What is the main reason leading to the difference between (a) and (b)? [5%]
- Given that the enthalpy of formation of X, CO₂, and H₂O are -75, -395, and -240 kJ/mol, respectively. The heat capacities (J/K-mol) of CO₂ and H₂O are $C_{p,CO_2} = 45 + 0.009 \times T$ and $C_{p,H_2O} = 30 + 0.01 \times T$, where T is the temperature with a unit of K. Assume the ideal gas law is applicable.

2. [15%] At 330 K, the electromotive force of a cell X|XY₂ (aq. 0.01 m), AgCl(s)|Ag is 0.75 V. The standard electromotive force of the cell is 0.55 V. Calculate the mean activity coefficient for the X²⁺ and Y⁻ ions by using

- (a) Nernst equation [5%]
- (b) Debye-Hückle limiting law [5%]
- (c) Comment on the potential reason causing the difference between these mean activity coefficients derived from the two methods. [5%]
3. [15%] The half-life of a molecule's first-order decomposition has been found to be 3450 s at 330 K and 500 s at 340 K. Assuming the Arrhenius equation is applicable. Calculate the following quantities:
- (a) Activation energy of the reaction [5%]
- (b) Enthalpy of activation at 330 K [5%]
- (c) Entropy of activation at 330 K [5%]

4. [15%] For a second-order irreversible reaction: A + B → P with initial concentrations of A, B, and P are [A]₀, [B]₀, and 0. The rate law of this reaction is: $d[A]/dt = -k_r[A][B]$.

- (a) Derive the relationship between [A], [B], and the reaction time t . [10%]
- (b) Derive the time constant (τ , representing the time taken for the concentration to 1/e of the initial value) of [A] with [A]₀ = 0.1 mol/L, [B]₀ = 0.2 mol/L, and the rate constant $k_r = 0.5 \text{ hr-L/mol}$. Note that e is Euler's number = 2.71828... [5%]

5. [15%] Based on the Langmuir adsorption isotherm of molecular hydrogen (H_2):
- (a) Derive the surface coverage of an adsorption isotherm with the dissociation of molecular hydrogen on tungsten-filament incandescent lamps. Given that the adsorption and desorption rate constants are k_a and k_d , and the partial pressure of molecular hydrogen is P_{H_2} . [5%]
- (b) Derive an expression for the rate of formation of hydrogen atoms (H) when molecular hydrogen is in contact with hot tungsten in the following mechanism: $H_{2(g)} + \text{bare site } S_{(\text{surface})} \rightarrow H-S_{(\text{surface})} + H_{(g)}$. Given that the rate constant of this reaction is k_r . [5%]
- (c) Draw a plot describing the relationship between the reaction rate and partial pressure of molecular hydrogen and the limiting rate at extremely low/high partial pressure of molecular hydrogen. [5%]
6. Answer the following statements that are true (O) or false (X) [Each 5%, 25% in total]:
- (a) Based on Graham's law of effusion, the effusion rate of a gas molecule is inverse to its molecular weight.
- (b) Based on the Maxwell-Boltzmann distribution, the most probable speed of a gas molecule is lower than its root-mean-square speed.
- (c) A phase transition of a solid melting can occur reversibly, so the change of entropy is zero.
- (d) The ideal solubility of acenes in benzene is positively correlated to their enthalpy of fusion and melting point.
- (e) From the Eyring equation, the reaction coordinate is a loose vibration mode described by the partition function, including the vibration energy during bond breaking.