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

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※ 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 CO_2 and H_2O:

$$X_{(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

(a) Derive the adiabatic flame temperature of system burned at constant volume in the amount of oxygen required to give complete combustion forming CO_2 and H_2O. **[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, CO_2, and H_2O are –75, –395, and –240 kJ/mol, respectively. The heat capacities (J/K-mol) of CO_2 and H_2O are $C_{p,CO2} = 45 + 0.009 \times T$ and $C_{p,H2O} = 30 + 0.01 \times T$, 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 $X|XY_2$ (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 X^{2+} 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 $k_r = 0.5$ hr-L/mol. Note that e is Euler's number = 2.71828... **[5%]**

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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_{H2}. **[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: $H_{2(g)}$ + bare site $S_{(surface)}$ → $H–S_{(surface)}$ + $H_{(g)}$. 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.