高雄醫學大學 97 學年度博士班招生考試 綜合化學 (有機) 試題第 / 頁

1 (8 pt) Define: 1) Kinetic Resolution 2) Regioselective Reaction 3) Sigmatropic Rearrangement 4) Birch Reduction

2 (7 pt) Show how Novocain, a painkiller used frequently by dentists, can be prepared from benzene.

3 (6 pt) Complete the following reactions:

4 (4 pt) Propose a mechanism for the following reaction:

高雄醫學大學 97 學年度博士班招生考試 綜合化學 (分析)

「綜合化學(分析)」(25分)

- 1 Ultraviolet-visible molecular absorption spectrometry is a very important technique for identifying compounds and, especially, for quantitative analysis. Please answer the following questions as detailed as possible.
 - (a) Write down the Beer's law and define each term in this law (5 分)
 - (b) Beer's law is a limiting law. Why? (10 \Re) (Hint PV = nRI is also a limiting law that can be more appropriately used for a gas, which is in the condition of low pressure or high temperature)
- 2. Ion-selective electrode (ISE) is a very important tool in determination of ionic species such as H⁺, Na⁺, K⁺, F⁻, and etc. Please answer the following questions as complete as possible.
 - (a) In a pH meter, a pH-sensitive electrode is employed to determine pH values Please define the principle of pH sensing in a pH meter. (5 分)
 - (b) A pH meter sometimes encounters 'alkaline error' when it was used to determine the pH value of a basic solution. What causes 'alkaline error'? (5 分)

1

高雄醫學大學 97 學年度博士班招生考試 綜合化學 (物化) 試題第2頁

- 1. Please explain the following terms in your words (a) uncertainty principle (b)

 Arrhenius equation (c) colligative properties (d) Franck-Condon principle (e)

 diffusion-controlled reaction. (10%)
- 2. Please describe the possible relaxation pathway from the first excited singlet state and from the first excited triplet state. (5%)
- 3. The chlorination of vinyl chloride, $C_2H_3Cl + Cl_2 \longrightarrow C_2H_3Cl_3$, is believed to proceed by the following mechanism:

$$\begin{aligned} &\operatorname{Cl}_2 \stackrel{k_1}{\longrightarrow} 2\operatorname{Cl} \bullet \\ &\operatorname{Cl} \bullet + \operatorname{C}_2\operatorname{H}_3\operatorname{Cl} \stackrel{k_2}{\longrightarrow} \operatorname{C}_2\operatorname{H}_3\operatorname{Cl}_2 \bullet \\ &\operatorname{C}_2\operatorname{H}_3\operatorname{Cl}_2 \bullet + \operatorname{Cl}_2 \stackrel{k_3}{\longrightarrow} \operatorname{C}_2\operatorname{H}_3\operatorname{Cl}_3 + \operatorname{Cl} \bullet \\ &\operatorname{C}_2\operatorname{H}_3\operatorname{Cl}_2 \bullet + \operatorname{C}_2\operatorname{H}_3\operatorname{Cl}_2 \bullet \stackrel{k_4}{\longrightarrow} \text{stable species} \end{aligned}$$

Using steady-state approximation, derive the rate law expression based on this mechanism. (5%)

4. A strong absorption of infrared radiation is observed for ¹H³⁵Cl at 2991 cm⁻¹. Calculate the force constant, k, for this molecule. (5%)

高雄醫學大學 97 學年度博士班招生考試 綜合化學 (無機)

- 1 Please describe the valence bond theory (VBT) and molecular orbital theory (MO). What are differences between these two theories?
- 2. Using crystal field theory (CFI) to discuss how the differences d orbital splitting between octahedral (ML₆) and tetrahedral (ML₄) transition metal complexes.
- 3 The 18 electron rule is often using to predict the stability of organometallic compounds. Please give an example to discuss how to use the 18 electron rule and why the 18 electron rule works for those organometallic compounds.
- 4 Hard Soft Acid Base (HSAB) theory is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. Please define the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species.
- 5. TiCl₂ is an ionic solid, whereas TiCl₄ is a molecular liquid at room temperature. Please discuss why the oxidation states will influence the physical properties