國立中山大學九十一學年度博士班招生考試試題

科目:综合化學【化學系】

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有機化學、無機化學、分析化學、物理化學 【四科任選二科作答】

有機化學

 Use appropriate reagents to complete the following transformations. Several steps may be needed for each transformation. (20 points)

II. Write down the mechanisms for the following reactions. (20 points)

III. Use the given compound to complete the synthesis. (10 points)

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無機化學

- 1. Build the qualitative M.O. energy level diagram for an octahedral ML₆ complex, considering only the σ type interaction. The valence shell d, s, and p orbitals of the central metal ion have the symmetry representations of t_{2g} , e_g , a_{1g} , and t_{1u} . The ligand group orbitals have the symmetry representations of a_{1g} , t_{1u} , and e_g . (18pts)
 - (a) Identify the symmetry representations for the valence shell orbitals of the metal ion.
 - (b) Draw the shape of each ligand group orbitals.
 - (c) Build the qualitative M.O. energy levels originated from the above orbitals.
 - (d) Indicate the part of M.O. that may also be rationalized by the Ligand Field theory.
- Iodine is sparingly soluble in water, but is soluble after adding NaI into it. Please explain.(4pts)
- 3. Indicate what parameter of NMR spectra might be used to distinguish the *cis* and *trans* isomers of [W(CO)₄(P(CH₃)₃)₂].(8pts)

以下選擇題爲單選題(每題4分)

- 4. $[Fe(SCN)(OH_2)_5]^{2+}_{(aq)}$ is the intermediate of the reaction of $[Co(NCS)(NH_3)_5]^{2+}_{(aq)} + Fe^{2+}_{(aq)}$.
 - (a) The reaction mechanism is I_d .
 - (b) The reaction mechanism is D.
 - (c) This is an outer sphere electron transfer reaction.
 - (d) This is an inner sphere electron transfer reaction.
 - (e) The product of this reaction is [Fe(SCN)(OH₂)₅]³⁺(aq).
- 5. Which one is not the d-block element?
 - (a) Y (b) Tc
- (c) Zr
- (d) Tl (e)Ta
- 6. Which process can give rise to the highest proportion of HD?
 - (a) $H_2 + D_2$ equilibrated over a platinum surface.
 - (b) D₂O + NaH.
 - (c) Electrolysis of HDO.
 - (d) $H_2 + D_2$ passed through palladium film.
 - (e) $CaHD + H_2O$.
- 7. Which of the following reactions is not adopted to produce hydrogen gas in industry?
 - (a) $CH_4 + H_2O \rightarrow CO + 3H_2$
- (b) $2H_2O \rightarrow 2H_2 + O_2$
- (c) $CO + H_2O \rightarrow CO_2 + H_2$
- (d) $C + 2H_2O \rightarrow CO_2 + 2H_2$
- (e) $2 \text{ HCl} + Zn \rightarrow ZnCl_2 + H_2$
- 8. Which one is not a spontaneous reaction?
 - (a) $Ce^{4+}_{(aq)} + Fe^{2+}_{(aq)}$
- (b) $TiO_{(s)} + HCl_{(aq)}$
- (c) $Rb_9O_{2(s)} + H_2O_{(1)}$
- (d) Na_(am) + CH₃OH_(l), am=ammonia.
- (e) $Fe^{2+}_{(aq)} + H_{2(g)}$

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分析化學

Note: Always use the correct significant figures in your calculations!!

(12%)1.Define the following terms:

- (a) Q-test
- (b) ppb
- (c) charging current
- (d) precision
- (8%) 2. For phosphoric acid (H_3PO_4), $pK_1 = 2.15$, $pK_2 = 7.20$, $pK_3 = 12.15$. If you want to make a buffer solution of pH 4.70,
 - (a) is phosphoric acid suitable to make this buffer? Why or why not?
 - (b) show the structure of phosphoric acid.
- (7%) 3.(a) Give the name (in English) and show the structure of EDTA, the most commonly used chelating agent.
 - (b) Show the corresponding structures of metal chelates formed between a metal ion (e.g., Ca²⁺) and EDTA.
- (7%) 4.AAS has been the most widely used method for the determination of single elements in analytical samples.
 - (a) What does AAS stand for (in English)?
 - (b) Explain what is meant by spectral interference and chemical interference in AAS.
- (8%) 5. Show the van Deemter equation and explain each term in the equation.
- (8%) 6. (a) In most electrochemical analysis, it is desirable to have a reference electrode in the system. Why?
 - (b) Name a commonly used reference electrode and show its schematic diagram.
 - (c) Give the half-cell reaction and the corresponding Nernst equation related to the reference electrode you mentioned above.

物理化學

Total 50 pts.

1. (Thermodynamics)

- (a) A certain battery runs a toy truck and becomes partially discharged. In the process, it performs a total of 117.0 joules of work (w) on its immediate surroundings. It also gives off 3.0 joules of heat (q), which the surroundings absorb. No other work or heat is exchanged with the surroundings. Compute q, w, and ΔU (internal energy) for the battery, making sure each quantity has the proper sign. (6 pts.)
- (b) The same battery is now recharged exactly to its original state. This requires 210.0 joules of electrical work from an generator. Determine q for the battery in this process. (5 pts.)
- (c) Explain why q has the sign that it does. (5 pts.)

2. (Chemical Kinetics)

- (d) Liquid A decomposes by first-order kinetics and 5% of A is converted in 5 minutes. How much longer would it take to reach 75% conversion? (8 pts.)
- (e) Repeat the previous problem for second-order kinetics. (8 pts.)

3. (Quantum Chemistry)

An extremely crude picture of an electron in an atom is to treat the electron as a particle in a one-dimensional box which has a length on the order of the size of the atom.

- (f) For an electron in a box of length 1.0 A, calculate the separation between the two lowest energy levels. (6 pts.)
- (g) Calculate the wavelength of a photon corresponding to a transition between these two levels. (6 pts.)
- (h) What portion of the electromagnetic spectrum does this wavelength correspond to? (6 pts.)

 $(m_e = 9.1 \times 10^{-31} \text{ kg}, h = 6.6262 \times 10^{-34} \text{ joule} \cdot \text{s}, c = 3 \times 10^8 \text{ m/s})$