有機化學部份 (共 50 分)

(20%) 一．選擇題（單選，每題 2 分，答錯不倒扣）

1. Which of the following compounds is the most acidic?
   (a) cyclohexene
   (b) 1-pentyne
   (c) tert-butyl alcohol
   (d) cyclopentadiene
   (e) toluene

2. Starting with 2-butene, which of the following is the best method for preparing 2-butyne?
   (a) HBr; H₂/Ni; Zn/H⁺
   (b) HBr; Zn/H⁺; H₂/Ni
   (c) Br₂/CCl₄; Zn/H⁺; H₂/Ni
   (d) HBr; 2 NaNH₂
   (e) Br₂/CCl₄; 2 NaNH₂

3. Which of the following lists the correct order of reactivity of the substrates in electrophilic aromatic substitution reactions?
   (a) pyrrole > furan > thiophene > benzene
   (b) thiophene > pyrrole > furan > benzene
   (c) benzene > furan > thiophene > pyrrole
   (d) furan > pyrrole > benzene > thiophene
   (e) pyrrole > benzene > thiophene > furan

4. Which of the following reducing agents is best used in the reaction shown below?
   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}_2\text{O}^-\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \]
   (a) LiAlH₄; H₃O⁺
   (b) Zn(Hg)/H⁺
   (c) NaBH₄; H₂O⁺
   (d) Na/NH₃
   (e) H₂/Raney Ni

5. Which of the following synthetic routes works best for preparing 4-octene?
   (a) 4-bromooctane + NaOCH₃
   (b) 4-bromooctane + NaOC(CH₃)₃
   (c) CH₃CH₂CH₂CH=PPh₃ + CH₃CH₂CH₂CHO
   (d) CH₃CH₂CH=PPH₃ + CH₃CH₂CH₂CH₂CHO
   (e) 4-fluoroctane + NaOCH₃
6. Which of the following m/z values is the base peak for benzyl alcohol?

(a) 17  
(b) 52  
(c) 77  
(d) 91  
(e) 108

7. Which compound’s carbonyl stretch occurs at the lowest wavenumber?

(a) CH₃CH₂CH₂CHO  
(b) CH₃CH₂CONH₂  
(c) CH₃CH₂CO₂CH₃  
(d) CH₃COCH₂CH₃  
(e) CH₃CH₂COCH₂CH₃

8. How many stereoisomers exist with the following basic connectivity?

CH₃CHCICH₂CHClCH₃  
(a) 0  
(b) 1  
(c) 2  
(d) 3  
(e) 4

9. (-)-Mandelic acid has a specific rotation of $-158^°$. What would be the specific rotation of a solution which contains 40% (-)-mandelic acid and 60% (+)-mandelic acid?

(a) $+95^°$  
(b) $+63^°$  
(c) $+32^°$  
(d) $-32^°$  
(e) $-63^°$

10. Which is the major product of the following reaction?

\[ \text{CH₃CH=CHCN} + \text{CH₂CN} \rightarrow ? \]

(a)  
(b)  
(c)  
(d)  
(e)
(20%) Identify the structure of the products A-J.

(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{Br}_2 \\
\text{hv} \\
\end{array}
\xrightarrow{\text{A}}
\begin{array}{c}
\text{O} \\
\text{OH} \\
\text{BH}_3, \text{THF} \\
\text{H}_2\text{O}_2, \text{HO}^- \\
\end{array}
\xrightarrow{\text{B}}
\begin{array}{c}
\text{C} \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{CCl}_3, \text{AlCl}_3 \\
\text{H}_2\text{O} \\
\end{array}
\xrightarrow{\text{D}}
\begin{array}{c}
\text{ROOH} \\
\text{E} \\
\end{array}
\]

(c) \[
\begin{array}{c}
\text{EtO}_2\text{C} \leftarrow \text{CO}_2\text{Et} \\
\text{1. NaOEt} \\
\text{2. H}_3\text{O}^+ \\
\end{array}
\xrightarrow{\text{F}}
\begin{array}{c}
\text{1. NaOEt} \\
\text{2. CH}_3\text{CH}_2\text{Br} \\
\text{3. H}^+, \text{H}_2\text{O}, \Delta \\
\end{array}
\xrightarrow{\text{G}}
\]

(d) \[
\begin{array}{c}
\text{t-Bu} \rightarrow \text{CH}_3 \\
\text{1. Na, NH}_3(\text{l}) \\
\text{2. aq. NH}_4\text{Cl} \\
\text{3. mCPBA, CH}_2\text{Cl}_2 \\
\end{array}
\xrightarrow{\text{H}}
\begin{array}{c}
\text{1. Li-C≡CH} \\
\text{THF} \\
\text{2. H}_2\text{O} \\
\end{array}
\xrightarrow{\text{I}}
\]

(e) \[
\begin{array}{c}
\text{3. Hg(OAc)}_2, \text{THF, H}_2\text{O} \\
\text{4. NaBH}_4, \text{NaOH, H}_2\text{O} \\
\end{array}
\xrightarrow{\text{J}}
\]

III. Show how the following compounds could be synthesized from the given starting materials?

(4%) (a) \[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{H} \\
\text{CH}_3 \\
\text{from} \\
\text{CH}_3 \\
\end{array}
\]

(3%) (b) \[
\begin{array}{c}
\text{H} \leftarrow \text{Br} \\
\text{HO} \leftarrow \text{H} \\
\text{CH}_3 \\
\text{from} \\
\text{HC≡CH} \\
\end{array}
\]

(3%) (c) \[
\begin{array}{c}
\text{from} \\
\text{EtO}_2\text{CCH}_2\text{CO}_2\text{Et} \\
\end{array}
\]
無機化學部分（共 50 分）

四. 配位化學（每題 5 分，共 15 分）
(a) Determine which of the following is paramagnetic. Explain your choice, and estimate its magnetic moment.

\[ \text{[Fe(CN)₆]^{4-}}, \text{[Co(H₂O)₆]^{3+}}, \text{[CoF₆]^{3-}}, \text{[RhF₆]^{3-}} \]

(b) Draw the molecular structure for the complex:

\( \text{mer-chloroethylenediaminetetraaminecobalt(III)} \)

(c) Sketch all isomers of the following complex. Indicate clearly each pair of enantiomers.

\( \text{[Pt(2,2'-bipyridine)BrCl]^{2+}} \)

五. 酸鹼化學（每題 5 分，共 10 分）
(a) Explain the "leveling effect" in acid-base chemistry.

(b) Arrange the order of basicity toward hydrogen ion for the following compounds.

pyridine  2-methylpyridine  2-butylpyridine  2,6-dimethylpyridine

六. 主群化學（每題 5 分，共 15 分）
(a) Potassium superoxide has been used in the self-contained breathing apparatus used by fire-fighter (to remove moisture and carbon dioxide from breathing and to produce oxygen). Explain what the reactions are.

(b) On the base of VSEPR model, predict the structure of XeOF₂ and assign its point group.

(c) In the laboratory, chlorine from photodecomposition of chlorofluorocarbon has been evidenced to catalyze the decomposition of ozone. Show the catalytic reactions.

七. 有機金屬化學（每題 5 分，共 10 分）
(a) What is the organic fragment isolobal with \( \text{[Mn(CO)₃]^+} \)?

(b) On the basis of the 18-electron rule, draw the molecular structure for \( \text{(C₃H₅)₂W(CO)₂} \).
ANALYTICAL CHEMISTRY

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

(10%) 1. Define the following terms:
   (a) pipet   (b) RSD   (c) chelating agent (name one)   (d) Beer’s Law

(7%) 2. The diprotic acid H₂A has pK₁ = 3.00 and pK₂ = 7.00.
   (a) What is a buffer solution?
   (b) Calculate the pH of a solution prepared by mixing 50.00 mL of 0.100 M H₂A with 40.00 mL of 0.200 M NaOH.
   (c) At what pH is [HA⁻] = [H₂A]? Why?

(5%) 3. (a) 93.1 MHz = ? Hz   (b) 21.6 nL = ? mL   (c) 0.100 mM Na⁺ = ? ppb Na⁺ (Na = 23.0)
   (d) How many significant figures are there in 0.03840?

(9%) 4. (a) What is fluorescence?
   (b) Explain the difference between a fluorescence emission spectrum and a fluorescence excitation spectrum. Which more closely resembles an absorption spectrum? Why?
   (c) Name the radiation source and the detector (or transducer) commonly used in the spectrofluorometer.

(7%) 5. (a) Give the full name of HPLC (in English).
   (b) What are the most commonly used stationary phase and mobile phase in reverse phase LC?
   (c) Predict the elution order of n-pentane and n-pentanol in reverse phase LC. Why?

(7%) 6. (a) What is Anodic Stripping Voltammetry (ASV)?
   (b) ASV is the most sensitive electroanalytical chemistry method for analysis of trace metal ions (e.g., Pb²⁺, Cd²⁺) in river water samples. Why?

(5%) 7. MALDI has been widely used in proteome study recently. What is MALDI?
8. (7%) Calculate the variation of chemical potential of ice when the pressure on ice increases from 1 bar to 2 bar. The density of ice is 0.917 g cm$^{-3}$.

9. (7%) The data below show the temperature variation of the equilibrium constant of the reaction: $\text{Ag}_2\text{CO}_3(\text{s}) \rightarrow \text{Ag}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$. Calculate the standard reaction enthalpy of the decomposition.

<table>
<thead>
<tr>
<th>T/K</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{eq}}$</td>
<td>0.000398</td>
<td>0.0141</td>
<td>0.186</td>
<td>1.48</td>
</tr>
</tbody>
</table>

10. (7%) The emission spectrum of atomic hydrogen shows line at 82.259, 97.492, 102.824, 105.292, 106.632, and 107.440 cm$^{-1}$, which correspond to transitions to the same lower state. Determine the ionization energy of the lower state. $E_{\text{ion}} = 1.9863 \times 10^{-16}$ erg

11. (7%) Calculate the ratio of populations ($N_\parallel / N_\perp$) for protons in the magnetic field of 10 T at 25°C. For proton, $g_\parallel = 5.586$, $\mu_N = 5.051 \times 10^{-27}$ J T$^{-1}$. $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$

12. (7%) The wavenumbers of the three normal modes of water are 3656.7, 1594.8 and 3755.8 cm$^{-1}$. Evaluate the vibrational partition function at 1500 K. Note: $\hbar/k = 0.69507$ cm$^{-1}$

13. (7%) What is the mean speed of nitrogen molecule in air at 25°C

14. (8%) Suppose that in an industrial batch process a substance $A$ produces the desired compound $I$ with rate constant $k_a$ which goes on to decay to a worthless product $C$ with rate constant $k_b$, each step of the reaction being first-order. At what time will $I$ be present in greatest concentration?