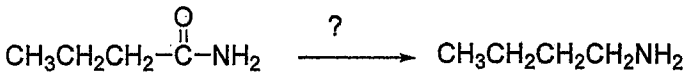
科目：有機化學及無機化學【化學系碩士班】 √

有機化學部份（共50分）

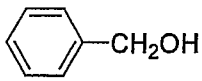
(20%) 一. 選擇題 (單選, 每題2分, 答錯不倒扣)

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; H_2/Ni; Zn/H^+
   (b) HBr; Zn/H^+; H_2/Ni
   (c) Br_2/CCl_4; Zn/H^+; H_2/Ni
   (d) HBr; 2 $NaNH_2$
   (e) Br_2/CCl_4; 2 $NaNH_2$
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?



   (a) $LiAlH_4$; H_3O^+
   (b) $Zn(Hg)/H^+$
   (c) $NaBH_4$; H_3O^+
   (d) Na/NH_3
   (e) H_2/Raney Ni
5. Which of the following synthetic routes works best for preparing 4-octene?
   (a) 4-bromooctane + $NaOCH_3$
   (b) 4-bromooctane + $NaOC(CH_3)_3$
   (c) $CH_3CH_3CH_2CH{=}PPh_3$ + $CH_3CH_2CH_2CHO$
   (d) $CH_3CH_2CH{=}PPh_3$ + $CH_3CH_2CH_2CH_2CHO$
   (e) 4-fluorooctane + $NaOCH_3$

6. Which of the following m/z values is the base peak for benzyl alcohol?



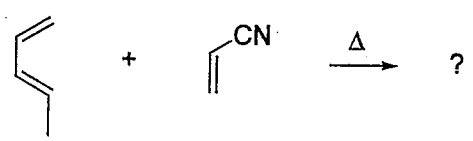
(a) 17
(b) 52
(c) 77
(d) 91
(e) 108

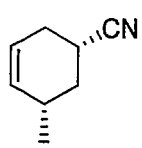
7. Which compound's carbonyl stretch occurs at the lowest wavenumber?
(a) $CH_3CH_2CH_2CHO$
(b) $CH_3CH_2CONH_2$
(c) $CH_3CH_2CO_2CH_3$
(d) $CH_3COCH_2CH_3$
(e) $CH_3CH_2COCH_2CH_3$

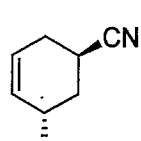
8. How many stereoisomers exist with the following basic connectivity?
$CH_3CHClCH_2CHClCH_3$
(a) 0
(b) 1
(c) 2
(d) 3
(e) 4

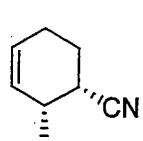
9. (-)-Mandelic acid has a specific rotation of –158°. What would be the specific rotation of a solution which contains 40% (-)-mandelic acid and 60% (+)-mandelic acid?
(a) +95°
(b) +63°
(c) +32°
(d) –32°
(e) –63°

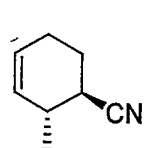
10. Which is the major product of the following reaction?

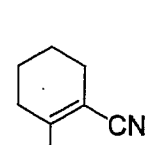


(a) 

(b) 

(c) 

(d) 

(e) 

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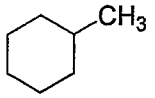
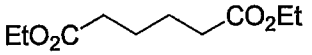
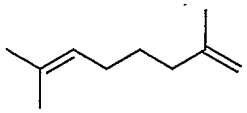
(20%) 二. Identify the structure of the products **A-J**.

(a)  $\xrightarrow[h\nu]{Br_2}$ **A** $\xrightarrow{^-OH}$ **B** $\xrightarrow[2.\ H_2O_2,\ HO^-]{1.\ BH_3,\ THF}$ **C**

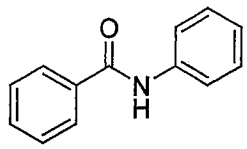
(b)  $\xrightarrow[2.\ H_2O]{1.\ CH_3\overset{O}{\overset{\|}{C}}Cl,\ AlCl_3}$ **D** $\xrightarrow{R\overset{O}{\overset{\|}{C}}OOH}$ **E**

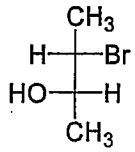
(c) EtO_2C  CO_2Et $\xrightarrow[2.\ H_3O^+]{1.\ NaOEt}$ **F** $\xrightarrow[3.\ H^+,\ H_2O,\ \Delta]{1.\ NaOEt\ \ 2.\ CH_3CH_2Br}$ **G**

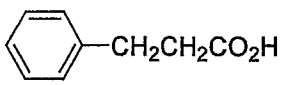
(d) *t*-Bu—≡—CH_3 $\xrightarrow[2.\ aq.\ NH_4Cl\ \ 3.\ mCPBA,\ CH_2Cl_2]{1.\ Na,\ NH_{3(l)}}$ **H** $\xrightarrow[2.\ H_2O]{1.\ Li—C\equiv CH\ \ THF}$ **I**

(e)  $\xrightarrow[4.\ NaBH_4,\ NaOH,\ H_2O]{1.\ Sia_2BH,\ THF\ \ 2.\ H_2O_2,\ NaOH\ \ 3.\ Hg(OAc)_2,\ THF,\ H_2O}$ **J**

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

(4%) (a)  from 

(3%) (b)  from $HC\equiv CH$

(3%) (c)  from $EtO_2CCH_2CO_2Et$

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無機化學部分 (共 50 分)

四、配位化學 (每小題 5 分； 共 15 分)

(a) Determine which of the following is paramagnetic. Explain your choice, and estimate its magnetic moment.

$[Fe(CN)_6]^{4-}$　　$[Co(H_2O)_6]^{3+}$　　$[CoF_6]^{3-}$　　$[RhF_6]^{3-}$

(b) Draw the molecular structure for the complex:
mer-chloroethylenediaminetriamminecobalt(III)

(c) Sketch all isomers of the following complex. Indicate clearly each pair of enantiomers.
$[Pt(2,2'\text{-bipyridine})BrCl]^{2+}$

五、酸鹼化學 (每小題 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-dimehylpyridine

六、主群化學 (每小題 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.

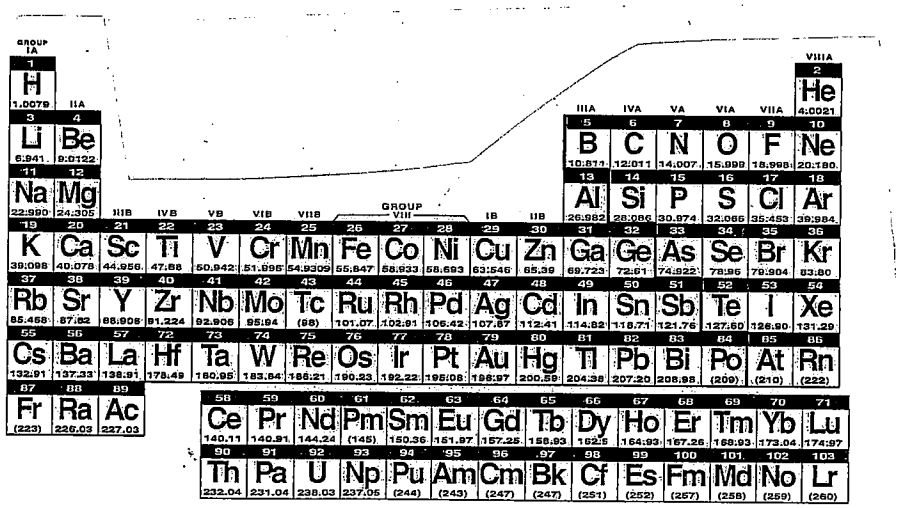
(b) On the base of VSEPR model, predict the structure of $XeOF_2$ and assign its point group.

(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 (每小題 5 分； 共 10 分)

(a) What is the organic fragment isolobal with $[Mn(CO)_5]^+$?

(b) On the basis of the 18-electron rule, draw the molecular structure for $(C_5H_5)_2W(CO)_2$.



科目：物理化學及分析化學【化學系碩士班】

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 H_2A has $pK_1 = 3.00$ and $pK_2 = 7.00$.

(a) What is a buffer solution?

(b) Calculate the pH of a solution prepared by mixing 50.00 mL of 0.100 M H_2A with 40.00 mL of 0.200 M NaOH.

(c) At what pH is $[HA^-] = [H_2A]$? 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 fluorescene 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., Pb^{2+}, Cd^{2+}) in river water samples. Why?

(5%) 7. MALDI has been widely used in proteome study recently. What is MALDI?

科目：物理化學及分析化學【化學系碩士班】

Physical Chemistry part

8. (7%)Calculate the variation of chemical potential of ice when the pressure on ice increases from 1bar to 2bar. The density of ice is 0.917g cm^{-3}.

9. (7%)The data below show the temperature variation of the equilibrium constant of the reaction: $Ag_2CO_{3(s)} \longrightarrow Ag_2O_{(s)} + CO_{2(g)}$. Calculate the standard reaction enthalpy of the decomposition.

T/K	350	400	450	500
$K_{equil.}$	0.000398	0.0141	0.186	1.48

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

11. (7%)Calculate the ratio of populations (N_β / N_α) for protons in the magnetic field of 10T at 25℃. For proton, $g_I = 5.586$, $\mu_N = 5.051 \times 10^{-27}\ J\ T^{-1}$. $k = 1.38 \cdot 10^{-23}\ J K^{-1}$

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 1500K. Note: k/hc = 0.69507 cm^{-1}

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

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?