中國文化大學八十七學年度碩士班入學考試

所(組)別：應用化學研究所　　考試科目：分析化學

Part A (65 points)　　Calculator Permit

1. The mercury in fish taken from Tam-Shui River was determined by a method based on the absorption of radiation by gaseous elemental mercury. Calculate a pooled estimate of the standard deviation for the method based on the following data:
   Hg content(ppm) 2.06, 1.93, 2.12, 2.16, 1.89, 1.95　(5%)
2. Please express the formulas of charge balance and mole balance (mass balance) of AgBr in 0.020M NH_3 solution, if the pertinent equilibria is:
   $AgBr = Ag^+ + Br^-$
   $Ag^+ + 2NH_3 = Ag(NH_3)_2^+$
   $NH_3 + H_2O = NH_4^+ + OH^-$　(10%)
3. What is the pH of a solution that is 0.055M in acetic acid (CH_3COOH) and 0.011M in sodium acetate (CH_3COONa)? Calculate the pH change of the buffer upon dilution by a factor of 100. The dissociation constant (K_a) is 1.8×10^{-5}.　(10%)
4. When 25ml of 0.10M acetic acid sample was titrated with 0.10M NaOH, Calculate pH of the sample (a) after added 10ml NaOH, (b) at the equivalent. The dissociation constant (K_a) is 1.8×10^{-5}.　(10%)
5. An ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving approximately 4g of the disodium salt in approximately 1 liter of water. An average of 42.35ml of this solution was required to titrate 50.0ml aliquots of a standard that contained 0.7682g of $MgCO_3$ (M.W.= 84.3g/mole) per liter. A 50.0ml aliquot of the mineral water was rendered strongly alkaline to precipitate the magnesium as $Mg(OH)_2$. Titration with a calcium-specific indicator required 31.54ml of the EDTA solution. Calculate (a) the molarity of the EDTA solution (b) the titer as mg-$CaCO_3$/ml in the mineral water. (10%)
6. Derive an expression for the equivalent-point potential for the reaction:
   $6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ = 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O$
   $Fe^{3+} + e^- = Fe^{2+}$
   $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- = 2\,Cr^{3+} + 7\,H_2O$
   These half reaction of redox potentials are expressed in $E_1(Fe^{3+}\text{-}Fe^{2+})$ and $E_2(Cr_2O_7^{2-}\text{-}Cr^{3+})$. (10%)
7. The cell SCE // H| (a = x) / glass electrode has a potential of 0.2094V when the solution in the right-hand compartment is a buffer of pH 4.006. The potential -0.3011V is obtained when the buffer is replaced with unknown. (a) Calculate the pH and the hydrogen ion activity of the unknown. (b) Assuming an uncertainty of ±0.002V in the junction potential, what is the range of pH within which the true value might be expected to lie?　(10%)

Part B (35%)

8. Explain or demonstrate terminology for the following (bold line portion):　(15%)
   (a) Zeeman background correction in graphite atomic absorbance spectrometry
   (b) gradient elution in high performance liquid chromatography
   (c) detection limit of analytic method
   (d) hydride generation method for metal determination
   (e) nuclear magnetic resonance(NMR)
9. Demonstrate the principles of thin layer chromatography(TLC) and, how do qualitative and quantitative samples which are measured by TLC. (10%)
10. Maxima exist at 470nm in the absorption spectrum for the bismuth(III)/thiourea complex and at 265nm in the spectrum for the bismuth(III)/EDTA complex. Predict the shape of a curve for the photometric titration of (a) bismuth(III) with thiourea(tu) at 470nm. (b) bismuth(III)/thiourea complex with EDTA at 265nm.
    $Bi(tu)_6^{+3} + H_2Y^{2-} = BiY^- + 6\,tu + 2\,H^+$　(10%)

(第一頁・共一頁)

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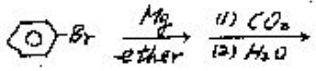
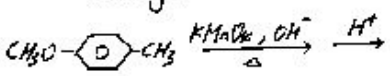
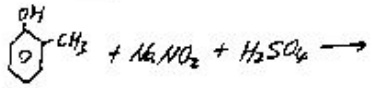
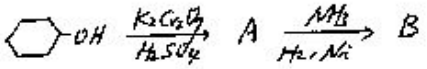
一、Give the major products of the following reactions: 76%
(每個答案4分，其中第5、8、10和11題有兩個答案)

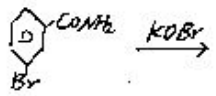
1. 

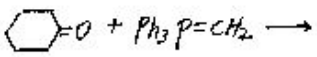
2. $RCN \xrightarrow[\text{catalyst}]{2H_2}$

3. 

4. 

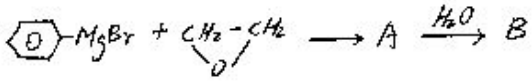
5. 

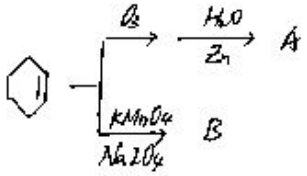
6. 

7. 

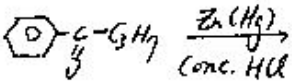
8. $CH_2CH(Br)-CH_2(Br) \xrightarrow{KOH(alc.)} A \xrightarrow{NaNH_2} B$

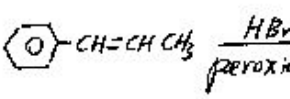
9. $CH_3CH_2CH_2MgBr + O=C(CH_3)(CH_3) \longrightarrow$

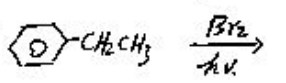
10. 

11. 

12. $CH_3-C\equiv C-H + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

13.  $\xrightarrow[Conc.\ HCl]{Zn(Hg)}$

14.  $\xrightarrow[peroxides]{HBr}$

15.  $\xrightarrow[h\nu]{Br_2}$

二. Which alcohol would you expect to be more easily dehydrated? $(CH_3)_2C(OH)CH_2CH_3$ or $(CH_3)_2CHCHOHCH_3$? 4%

三. Which is an extremely weak base?  or  ? 5%

四. Give the major products of reaction $CH_2=CH-CH=CH_2 + HBr$ at -80°C and 40°C respectively. 5%

五. Rank the following compounds in order of increasing acidity. CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH. 5%

六. Give the reactivity order in esterification of the following compounds:
CH_3COOH, RCH_2COOH, $R_2CHCOOH$, R_3CCOOH 5%

中國文化大學八十七學年度碩士班入學考試	
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20% 一. For each of the following compounds:

10% (a) Predict the shape by using VSEPR theory

10% (b) Decide the point group

(1) XeF_2 (2) PF_3

20% 二. List the following acids in order of acid strength in aqueous solution.

10% (a) HBr $HBrO$ $HBrO_2$ $HBrO_3$ $HBrO_4$

10% (b) H_2O PH_3 NH_3

10% 三. Give chemical names for the following:

(a) $K_4Fe(CN)_6$ (b) $Na[PtBrCl_2(C_2H_4)]$.

40% 四. For each of the following complexes

10% (a) Find the number of unpaired electrons

10% (b) Decide the magnetic moment

10% (c) Identify the ground-state term

10% (d) Calculate the ligand field stabilization energy.

(1) $Cr(CN)_6^{4-}$ (2) MnO_4^-

10% 五. Classify the following as labile or inert.

(1) $[Co(H_2O)_6]^{3+}$ (2) $[Fe(NH_3)]^{2+}$

(Explain your answer.)

中國文化大學八十七學年度碩士班入學考試	
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1. (12 points)

a. Show the relation between the Helmholtz energy and the maximum work done in a process

b. Show the relation between the Gibbs energy and the maximum non-expansion work

2. (10 points)

a. Calculate the equilibrium constant for the synthesis of a ammonia at 298 K

b. Estimate its value at 500 K

$N_{2(g)} + 3H_{2(g)} \dashrightarrow 2NH_{3(g)}$

	$NH_{3(g)}$	$N_{2(g)}$	$H_{2(g)}$
ΔH° (kJ mol^{-1})	-46.11		
S° (J K^{-1} mol^{-1})	192.45	191.61	130.684
ΔG° (kJ mol^{-1})	-16.45		

3. (14 points)

a. Explain the Michaelis-Menten mechanism of a enzyme action

b. Explain the Lindemann-Hinshelwood mechamism

4. (14 points)

Account for the rate law for the decomposition of N_2O_5

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)} \qquad \text{Rate} = k[N_2O_5]$$

on the basis of the following mechanism:

$N_2O_5 \longrightarrow NO_2 + NO_3$ $\quad k_a$

$NO_2 + NO_3 \longrightarrow N_2O_5$ $\quad k_a'$

$NO_2 + NO_3 \longrightarrow NO_2 + O_2 + NO$ $\quad k_b$

$NO + N_2O_5 \longrightarrow 3NO_2$ $\quad k_c$

5. (10%) Discuss the population ratio between the ground state and 1st excited state of vibrational energy for any gas molecule at room temperature and 1000K.

6. (20%) Describe (a) rotational constant and (b) Frank-Condon principle.

7. (20%) The length of hexatriene (with 6 pi electrons) is about 8.67 A, show that the first electronic transition is predicted to occur at 28000 cm^{-1}.

中國文化大學八十七學年度碩士班入學考試	
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1. Describe the difference of glycogen breakdown in the liver and muscle. What is the physiological significance? (15%)

2. Describe the membrane structure and the lipid motion within the bilayer of the membrane. (15%)

3. How does the DNA replication in the lagging strand go? (15%)

4. What is the wobble hypothesis in the process of RNA translation? What is its significance? (20%)

5. Explain the following terms. (20%)
(a) prosthetic group
(b) exon
(c) cytosol
(d) nucleosome

6. Using the information below, determine the sequence of a peptide. Explain how your structure is consistent with each piece of information. (15%)
(a) Complete hydrolysis by 1 M HCl at 110℃ followed by amino acid analysis indicated the presence of Gly, Leu, Phe and Tyr, in a 2:1:1:1 molar ratio.
(b) Treatment of the peptide with 1-fluoro-2,4-dinitrobenzene followed by complete hydrolysis and chromatography indicated the presence of the 2,4-dinitrophenyl derivative of tyrosine. No free tyrosine could be found.
(c) Complete digestion of the peptide with pepsin followed by chromatography yielded a dipeptide containing Phe and Leu, plus a tripeptide containing Tyr and Gly in a 1:2 ratio.