國立中山大學99學年度碩士班招生考試試題

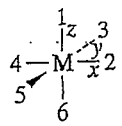
科目：有機化學及無機化學【化學系碩士班】

本試題分無機化學及有機化學兩部份，每部份各 50 分，總分 100 分。答案請依試題之先後順序，寫在答案紙上；否則，該題不予計分。

無機化學

1. Draw the chemical structures of the following compounds. (3x3 points)
   (1) μ-amido-μ-hydroxobis(tetraamminecobalt)(4+)
   (2) Δ-$[Ru(bipy)_3]^{2+}$
   (3) NbF_7^-
   Note: Bipy is the 2,2'-bipyridine.

2. Given a compound with an octahedral structure as shown in the following drawing and the table of sigma interactions for the d-orbitals in terms of angular overlap model, express the splitting energy of Δ_o, contributed only from the σ interaction in ligand field theory, by the parameter e_σ. (Show your work; otherwise, your answer will not be counted.) (4 points)

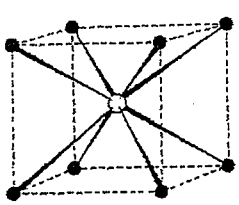


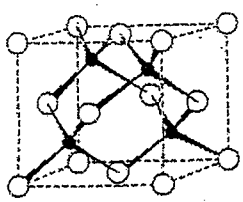
Octahedral positions

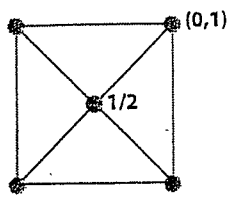
Sigma Interactions (all in units of e_σ)
Metal d Orbital

Ligand Position	z^2	x^2-y^2	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0

3. The unit cells of cesium chloride and zinc blende are shown in the following drawings. The cesium chloride may also be expressed by the right drawing (c). (2 x 2 points)
   (1) Draw the zinc blende in the same way as used in drawing (c).
   (2) Unit cells are classified to seven classes. What class does the cesium chloride belong to?


(a) Cesium chloride


(b) Zinc blende



(c) Cesium chloride

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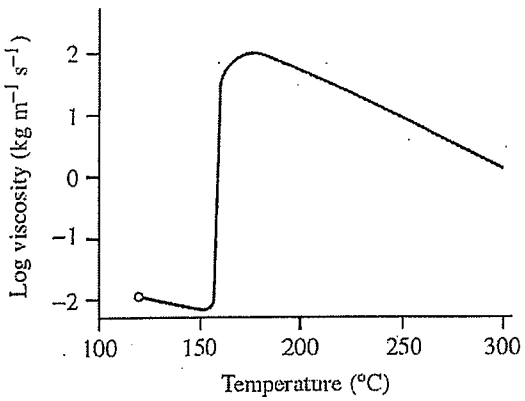
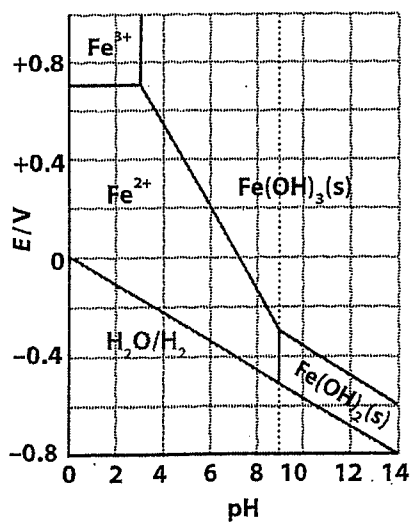
4. When sulfur is melting, the viscosity of the melted fluid varied with temperature. The following graph shows the temperature dependent viscosity of sulfur. Explain what happened to the sulfur molecules for showing this behavior. (6 points)



5. The following graph is the pH dependent redox potential for $Fe^{2+}(aq)$. Usually, this type of expression is called the Pourbaix diagram. (3 x 3 points)
   (1) What is the slope of the line between the Fe^{2+} and the $Fe(OH)_3(s)$ areas? (Show your work.)
   (2) What is indicated by the vertical dash line at about pH9?
   (3) The lowest line shows the various reduction potentials of H_2O/H_2 redox couple. Sketch this diagram on your answer sheet and draw a line to express the various reduction potentials of O_2/H_2O redox couple. (The potential of the half reaction, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$, is 1.23 volt at pH0.)



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6. Predict the products and balance the chemical equations for the following reactions. Ignore the physical state of each species. (4 x 2 points)
   (1) $CaC_2 + H_2O \rightarrow$
   (2) $ZnO + LiC_4H_9 \rightarrow$
   (3) $(CH_3)Mn(CO)_5 + CO \rightarrow$
   (4) $FeCl_2 + NaC_5H_5 \rightarrow$

7. Assume that A_3 is a linear triatomic molecule and the atom A has only one valence electron. (5x2 points)
   (1) What is the point group of the A_3 molecule?
   (2) If those atoms only use 1s orbitals to form chemical bonds, use appropriate SALC of those 1s orbitals to make the molecular orbitals. Ignore the work of normalization.
   (3) Draw the energy level diagram of those molecular orbitals with appropriate symmetry labels on them.
   (4) What is the bond order of the A_3 molecule?
   (5) Express the A_3 molecule with the most appropriate Lewis structure.
   Note: Character tables for several point groups are given as follows:

$C_{\infty v}$	E	C_2	$2C_\infty^\phi$	…	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	1	…	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	1	…	−1	R_z	
$E_1 \equiv \Pi$	2	−2	$2\cos\phi$	…	0	(x,y) (R_x,R_y)	(xz, yz)
$E_2 \equiv \Delta$	2	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
$E_3 \equiv \Phi$	2	−2	$2\cos 3\phi$	…	0		
…	…	…	…	…	…		
…	…	…	…	…	…		

$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…	1	−1	−1	…	−1	z	
Σ_u^-	1	1	…	−1	−1	−1	…	1		
Π_u	2	$2\cos\phi$	…	0	−2	$2\cos\phi$	…	0	(x,y)	
Δ_u	2	$2\cos 2\phi$	…	0	−2	$-2\cos 2\phi$	…	0		
…	…	…	…	…	…	…	…	…		

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D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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科目：有機化學及無機化學【化學系碩士班】

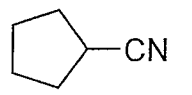
有機化學

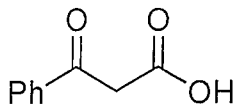
8. Define and give an example for each of the following terms. (10 pts.)

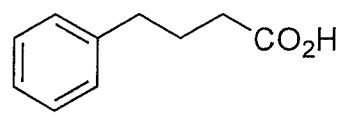
(a) Zaitsev's rule on elimination reaction (b) Claisen condensation (c) The endo rule on Diels-Alder reaction (d) Grignard reagent (e) Carbene

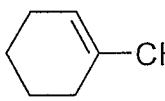
9. Predict the major products (including stereochemistry) of the following reactions. (20 pts)

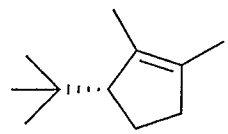
(a) $RCO_2H \xrightarrow{CH_2N_2}$

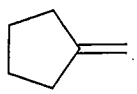
(b)  $\xrightarrow[2.\ H_3O^+]{1.\ CH_3MgI}$

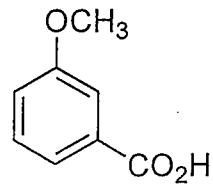
(c)  $\xrightarrow[2.\ H_2O]{1.\ LiAlH_4}$

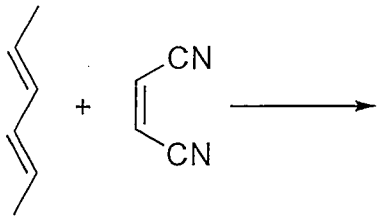
(d)  $\xrightarrow[2.\ AlCl_3]{1.\ SOCl_2}$

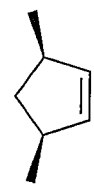
(e)  $\xrightarrow[(warm.,\ conc.)]{KMnO_4,\ H_2O}$

(f)  $\xrightarrow[Pt]{H_2}$

(g)  $\xrightarrow[H_2SO_4]{H_2O}$

(h)  $\xrightarrow[NH_3\ (L)]{Na}$

(i) 

(j)  $\xrightarrow[ROOH]{OsO_4}$

10. Give the structures of the following compounds. (10 pts.)

(a) (S)-6-Hydroxy-2-heptanone (b) (1R, 2R)-2-Methylcyclohexanol

(c) Benzylamine (d) 3-Oxopentanal (e) Cyclopentanecarbaldehyde

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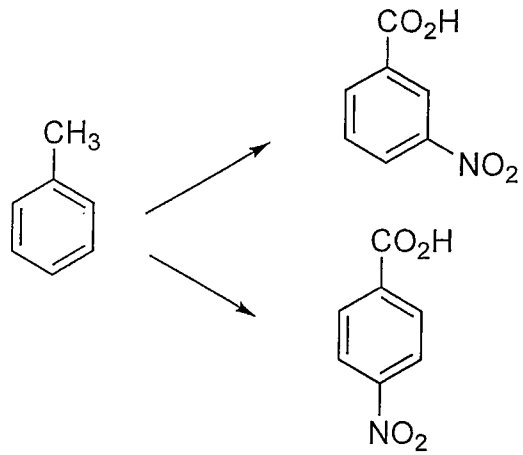
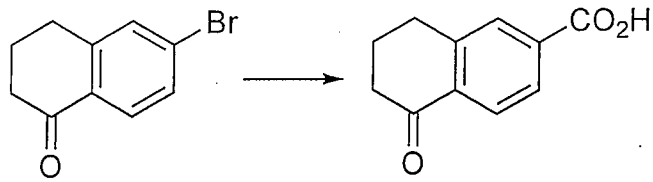
11. Accomplish the following syntheses. (you may use any necessary reagents) (10 pts.)

(a)



(b)



國立中山大學99學年度碩士班招生考試試題

科目：物理化學及分析化學【化學系碩士班】

Physical Chemistry Part

1. (13 %)The spin matrices for a nucleus with spin quantum number l are

$$I_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},\quad I_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix},\quad I_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

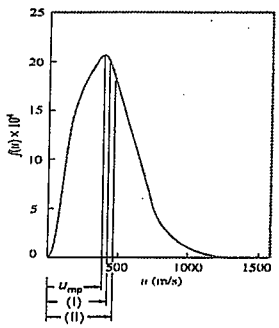
(i) Find the $[I_x, I_y]$, $[I_y, I_z]$, $[I_z, I_x]$

(ii) Find $I_x^2 + I_y^2 + I_z^2$

2. (9 %)Some water is placed in a coffee cup calorimeter. When 1.0 g of an ionic solid is added, the temperature of the solution increases from 21.5°C to 24.2°C as the solid dissolves. For the dissolving process, what are the signs (positive or negative) for ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}?

3. (10 %) A 0.1964 g sample of quinone ($C_6H_4O_2$) is burned in a bomb calorimeter that has a heat capacity of 1.56 kJ/°C. The temperature of the calorimeter increases by 3.2°C. Calculate the energy of combustion of quinone per gram and per mole. (Significant digit: 2)

4. (12 %) A velocity distribution for nitrogen gas at 273 K, with the values of most probable velocity (u_{mp}, the velocity at the curve maximum), the average velocity (u_{avg}), and the root mean square velocity (u_{rms}). What is the value of u_{avg} ? What is the value of u_{rms} ? Please link the u_{avg} and u_{rms} values with below figure (I) and (II). (That is, $u_{rms} > u_{avg}$ or $u_{avg} > u_{rms}$) (R = 8.314 Joule/mol · K; k =1.38×10^{-23} J/K)



5. (6 %)Which of the statements are accurate? (multiple choices)

(I)Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C).

(II)The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds.

(III)Hydrogen bonding also plays an important role in determining the three-dimensional structures adopted by proteins and nucleic bases.

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Analytical Chemistry Part (50%)

6. How many milliliters of 0.800 M KOH should be added to 3.38 g of oxalic acid [$(COOH)_2$] to give a pH of 4.40 when diluted to 500 mL? oxalic acid, 90.035 g/mol, $pK_1 = 1.27$, $pK_2 = 4.266$. (9%)

7. Calculate the thermodynamic potential of the following cell. Write the net cell reaction and state whether it is spontaneous in the forward or reverse direction. (10%)

   $Pt \mid U^{4+}$ (0.200 M), UO_2^{2+} (0.0150 M), H^+ (0.0300 M) ‖ Fe^{2+} (0.0100 M), Fe^{3+} (0.0250 M) $\mid$ Pt

   $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^0 = 0.771$ V

   $UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$ $\quad E^0 = 0.334$ V

8. A solution contains 35.3 μg/mL Cr (51.996 g/mol). The Cr is present only as dichromate ($Cr_2O_7^{2-}$) in 1.0 M H_2SO_4. The transmittance of this solution was 76.2% at 440 nm in a 1-cm pathlength cell. What is the molar absorptivity of dichromate at 440 nm? (7%)

9. Define the following terms
   (a) standard addition method
   (b) ionization suppressor in atomic spectroscopy
   (c) Stokes shift in Raman Spectroscopy
   (d) electrospray ionization (ESI)
   (e) selectivity factor
   (f) reversed-phase chromatography (4% each, 24% total)