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科目：無機化學(1003)

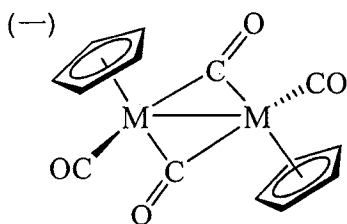
校系所組：中央大學化學學系

交通大學應用化學系 (甲組)

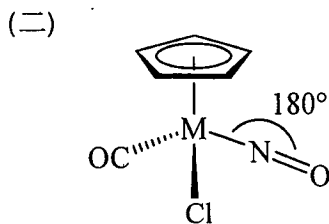
清華大學化學系

清華大學材料科學工程學系 (丙組)

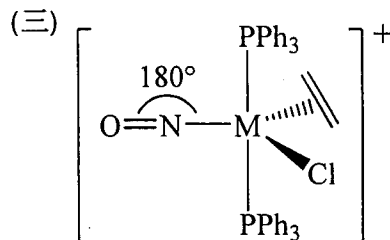
一、Write down the following parameters if the complexes shown below meet the 18-electron rule. (15%)



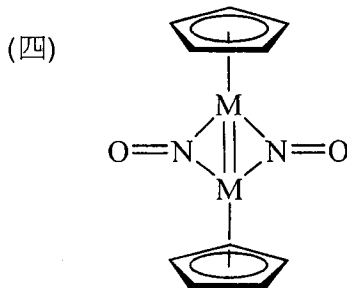
M: the first row transition metal



M: the second row transition metal

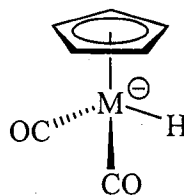


M: the third row transition metal



What is M for the first row transition metal?

(五)

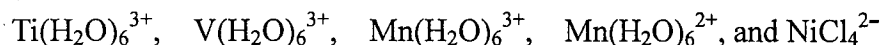


What is M for the second row transition metal?

二、Briefly answer the following questions.

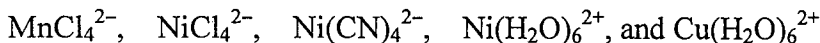
(一) Show the splitting of the metal d orbitals for square planar and trigonal bipyramidal complexes. (4%)

(二) Select the one that shows the weakest intensities for d-d transitions from the following complexes and give your reasons. (3%)



(三) Select the one that has the strongest d-d transition intensities from the following complexes.

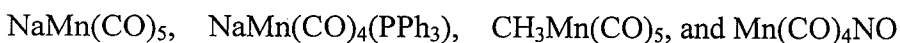
Give your reasons. (3%)



三、Briefly answer the following questions.

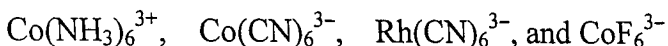
(一) Arrange the $\nu(\text{C}=\text{O})$ vibration frequencies in the increasing order for the following complexes.

Give your reasons. (4%)

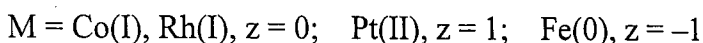


(二) Arrange the values of $10 Dq$ in the decreasing order for the following complexes.

Give your reasons. (3%)



(三) Arrange the tendency of being square planar complexes with the formula $\text{MCl}(\text{PPh}_3)_3^{z+}$. (3%)



注：背面有試題
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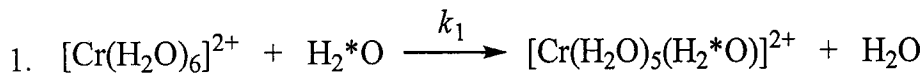
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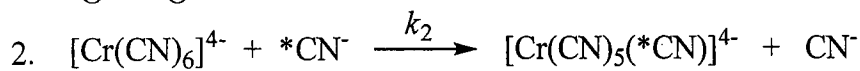
四、Briefly answer the following questions.

(一) Which one has larger k value?

(4%)



*O = ^{18}O

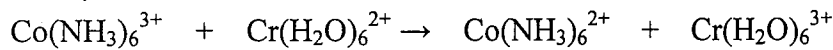


*C = ^{13}C

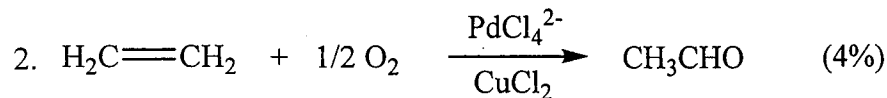
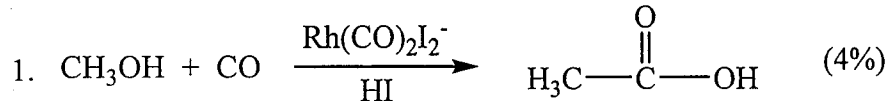
(二) Do you expect an inner-sphere or outer-sphere reaction mechanism for the following reaction.

Give your reasons.

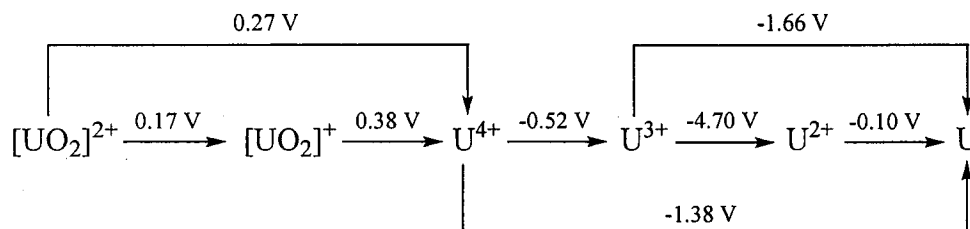
(3%)



(三) Write down the detailed reaction mechanism for the following two reactions.



五、The following potential diagram summarizes the results of electrochemical studies of the acidic aqueous solution chemistry of uranium.



(一) Based on the potential diagram shown above, draw the corresponding Frost diagram.

(5%)

(二) What is the most stable oxidation state of uranium in acidic aqueous solution?

(2%)

(三) Which species is (or are) thermodynamically unstable with respect to disproportionation?

(3%)

注意：背面有試題

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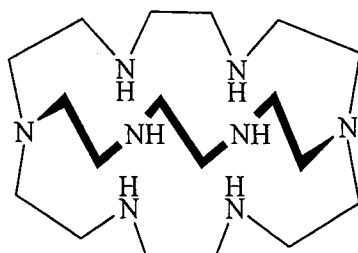
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- 六、The first barium sodide, $[\text{Ba}^{2+}(\text{H5-Azacryptand}[2.2.2])][\text{Na}^-]$, was synthesized by the reaction of Ba, Na, and H6-Azacryptand[2.2.2] (shown below). In the solid state, the Na^- ions pair up to give $[\text{Na}_2]^{2-}$. Construct an MO diagram for $[\text{Na}_2]^{2-}$ and determine the bond order in this species. (5%)



H6-Azacryptand[2.2.2]

- 七、(一) Write an equation for the reaction of NOCl with AgNO_3 in liquid N_2O_4 . What type of reaction is this? Explain? (6%)
- (二) Write a balanced equation for the oxidation of Mn^{2+} to MnO_4^- by the perxenate ion in acidic solution; Assume that neutral xenon is produced. (4%)
- 八、As shown below, each compound in List 1 has a matching description in List 2. Correctly match the partners. There is only one correct statement for each compound. (10%)

List 1	List 2
Li_3N	Sparingly soluble in water
CaF_2	Strong oxidizing agent
$\text{Be}(\text{OH})_2$	Formed by direct combination of the elements, and possesses a layer structure
Cs_7O	Amphoteric
Li_2CO_3	Polymeric in the solid state
NaBH_4	Soda lime
CaCl_2	A suboxide
MgO_2	A prototype crystal structure
BeCl_2	Hygroscopic solid, used for de-icing
$\text{Ca}(\text{OH})_2/\text{NaOH}$	Used as a reducing agent

注意：背面有試題

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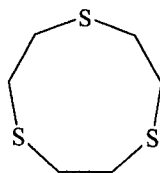
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九、A 6-coordinate complex may be obtained by crystallizing anhydrous CaI_2 from THF ($\text{C}_4\text{H}_8\text{O}$) solution at 253 K. In contrast, when anhydrous BaI_2 is crystallized from THF at 253 K, a 7-coordinate complex is isolated. Suggest structures for the two complexes. Rationalize why CaI_2 and BaI_2 in THF solutions form complexes that have different coordination numbers.

(5%)

十、The electronic spectra of mixtures of CH_2Cl_2 solutions (each 0.993 mmol/mL) of I_2 and the donor D shown below were recorded for different volume ratios of the two solutions. Values of the absorbance for the absorption at $\lambda_{\text{max}} = 308 \text{ nm}$ are as follows:

Volume ratio $\text{I}_2 : \text{D}$	Absorbance
0 : 10	0.000
1 : 9	0.056
2 : 8	0.097
3 : 7	0.129
4 : 6	0.150
5 : 5	0.164
6 : 4	0.142
7 : 3	0.130
8 : 2	0.103
9 : 1	0.070
10 : 0	0.000



Donor, D

(一) Suggest how compound D might interact with I_2 . (3%)

(二) Use the data in the table to establish the stoichiometry of the complex formed between D and I_2 . (3%)

(三) In the Raman spectrum of the complex, a band at 162 cm^{-1} is assigned to the I_2 stretching mode. Explain why this value is shifted from that of 215 cm^{-1} for I_2 itself. (4%)