

系所組別： 化學系

考試科目： 無機化學

考試日期： 0223，節次： 3

※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

注意：不須要依序答題，但是，題號務必寫清楚。

- (1) Explain why $\angle\text{H-C-H}$ (119.9°) of ethene ($\text{H}_2\text{C}=\text{CH}_2$) is larger than that of 116.5° for formaldehyde (H_2CO) (6%).
- (2) Based on VSEPR (Valence-Shell Electron-Pair Repulsion) theory, explain why an ion, TeCl_6^{2-} , adopts a geometric shape as a regular octahedron, rather than a distorted octahedron (6%).
- (3) Explain why NiCl_4^{2-} is a square-planar ion, whereas $\text{Ni}(\text{CO})_4$ is a tetrahedral molecule (6%).
- (4) Which kinds of the symmetry elements can make a molecule achiral? (6%)
- (5) Explain why a bridging carbonyl group of a dinuclear metal carbonyl compound (for example, $\text{Mn}_2(\text{CO})_{10}$) displays a smaller ν_{CO} frequency (in cm^{-1}) than a terminal carbonyl group (6%).
- (6) Explain why a neutral molecule, C_2 , has a shorter bond length than a cationic molecule, C_2^+ , whereas the reverse is true for O_2 and O_2^+ (8%).
- (7) A student tried to use ZnO as an oxidization reagent to prepare n-octane from n-BuLi. However, he did not obtain n-octane from the reaction. Instead, what he obtained is ZnBu_2 . Explain why he obtained such an unexpected result (6%).
- (8) A student wants to produce $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{CF}_3)$ from $\text{K}^+(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$. Suggest a suitable electrophilic reagent for him (4%) and write a reasonable reaction route, leading to the desired product (4%).
- (9) Although a singlet signal is observed at room temperature in the ^{19}F NMR spectrum of ClF_3 , the signal becomes complicated at -60°C . Draw a possible NMR pattern for the ^{19}F NMR multiplet at the temperature (^{19}F at 100% natural abundance with $I = 1/2$) (6%).
- (10) Transition-metal d-d transition is Laporte (orbitally) forbidden and a transition-metal complex is usually lightly colored in solution. Explain why KMnO_4 dissolves in water and becomes a deep blue solution (6%).
- (11) The reaction of CrCl_3 with PhLi is complicated. One neutral product contains one chromium atom and four Ph groups. Based on the 18-electron rule, draw a possible structure and give your reason (6%).
- (12) Write an IUPAC name for $\text{K}_2[\text{Fe}(\text{en})_2(\text{CN})_2]$ (4%), write the electron configuration in a crystal field and calculate the related crystal field stabilization energy in Dq values (6%).
- (13) One student found that the reaction of $\text{Fe}(\text{CO})_5$ with Me_3NO produced $\text{Fe}(\text{CO})_4(\text{NMe}_3)$ and CO_2 . Propose a detailed mechanism (8%).
- (14) Which one of two similar reactions occurs more rapidly and give your reasoning:
 - (a) The oxidative addition of $[\text{Co}(\text{dppe})_2]^+$ or $[\text{Ir}(\text{dppe})_2]^+$ with H_2 (6%).
 - (b) The migratory insertion of $[\text{CpMo}(\text{CO})_3\text{Me}]$ or $[\text{CpMo}(\text{CO})_3(\text{CF}_3)]$ with PPh_3 (6%).