國立成功大學 80 學年度化學研究所試(無機化學試題)其

- 1. On the basis of inductive effect, the Lewis acidity of the boron halides is expected to be $BF_3 > BCI_3 > BBr_3$. Experimentally, the opposite is observed. Explain these apparent anomaly (5%).
- 2. Complete the following equations: (8%)

(a)
$$2 \text{ CrO}_4^{2^-} + 2 \text{ H}_3 \text{O}^+ \longrightarrow$$

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$$2 \text{ CrO}_4^{2^-} + 2 \text{ H}_3\text{O}^+ \longrightarrow$$

(b) $(\text{H}_3\text{Si})_2\text{O} + \text{BF}_3 \longrightarrow$
(c) $\text{B}_4\text{H}_{10} + 2 (\text{CH}_3)_3\text{N} \longrightarrow$

- 3. Explain the following: (12%)
- (a) Borazines undergo addition reactions much more easily than does benzene.
- (b) The optical absorption bands of lanthanide compounds are much narrower than those of transition complexes.
- (c) Trisilylamine, (H₃Si)₃N, is a very weak base.
- (d) Si₂H₆ is more chemically reactive than does C₂H₆.
- 4. Use the Valence Bond theory to predict the structure of NO 2, NO 2+, and NO 2 (including the assignment of lone-paired electrons) (6%).
- 5. The melting point of following compounds shown as below: KBr, 730°C; CsF, 684°C; CaBr₂, 765°C; BaF₂, 1280°C Explain the trend of changing (4%).
- 6. Predict the trend of IR stretching frequency of C=O in the following compounds
- (a) cyclobutanone (b) cyclopentanone (c) cyclohexanone
- 7. Give the ground-state term symbol of Cr3+, Mg, and C with consideration of the spin-orbit coupling effect (6%).
- 8. Use Slater's rule and Clementi & Raimondi Equation to evaluate the effective nuclear charge (Z) for a 2S-electron of Br atom, respectively. Explain the difference between the two values of Z (5%). [Clementi & Raimondi Equation of shielding factor: $S_{2s} = 1.7208 + 0.3601 (N_{2s} - 1 + N_{2p}) + 0.2062 (N_{3s,p,d} + N_{4s,p})$

9. Tell the difference between lability and instability of a compound (3%).

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10. Give possible structures of $[Pt(NH_3)_2(py)_2Cl_2]^{2+}$ (3%).

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- 11. From the view points of Valence Bond Theory and Molecular Orbital Theory, what would make CO a very strong ligand? (8%)
- 12. Using the following data, illustrate what kind of relationship exists between the acid-base strength and hardness (or softness) (5%).

F + H⁺ <----> HF
$$K_{eq} = 10^{2.85}$$
 Cl + H⁺ <----> HCl $K_{eq} = 10^{-7}$ S^2 + H⁺ <----> HS $K_{eq} = 10^{14.2}$ $K_{eq} = 10^{14.2}$ F + CH₃Hg⁺ <----> CH₃HgF $K_{eq} = 10^{1.5}$ Cl + CH₃Hg⁺ <----> CH₃HgCl $K_{eq} = 10^{5.25}$ $K_{eq} = 10^{21.2}$

- 13. The ground state for a d 1 species is 2 D. What states will 2 D be split into if a d 1 species is under the influence of a tetrahedral field? What electronic configurations will correspond to each split state? How many microstates does each split state contain? (6%)
- 14. Draw structures for (a) π -allylmolybdenum (b) $Os_3(CO)_{10}(\mu_2\text{-CH}_2)(\mu_2\text{-CO})$ (c) Metalacyclobutane (6%).
- 15. Explain the following questions:
- (a) β -Elimination cannot happen for Cr(CHMe $_2$) $_4$ although this compound has β -hydrogen atoms (3%).
- (b) The reaction between $(\eta^5-C_5\text{Me}_5)_2\text{Zr}(\text{Me})_2$ and CO does not give the expected product, $(\eta^5-C_5\text{Me}_5)_2\text{Zr}(\text{Me})(\eta^1-\text{acyl})$ but $(\eta^5-C_5\text{Me}_5)_2\text{Zr}(\text{Me})(\eta^2-\text{acyl})$ (3%).
- (c) W(CO)(PhC₂Ph)₃ is an eighteen-electron compound although each diphenylacetylene can donate four electrons to the tungsten atom (2%).
- (d) $L_2TiCl_3(CH_2CH_3)$ (L is a phosphorus ligand) contains an agostic ethyl group; this group is stable with respect to β -elimination (3%).
- 16. Give the electron counts for the following compounds: (8%)
- (a) WMe_6 (b) $Co(\eta^5-C_5H_5)_2$ (c) $Mn(CO)_5$ (d) $Cr(NO)_4$.