國立中央大學八十六學年度碩士班研究生入學試題卷

1. The Pk value for arsenious acid, H_3AsO_3, is 9.2 and that for hypophosphorus acid, H_3PO_2, is ~1. What structures are consistent with these values ? (6%)

2. The 18e rule is a way to help us decide whether a give d-block transition metal organometallic complex is likely to be stable. please give three complexes with 18e, and also three complexes without 18e but stable. (12%)

3. In the presence of a base; OH^-, hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ gives Cl displacement product; $[Co(NH_3)_5OH]^{2+}$. Please propose a mechanism for this substitution reaction. (10%)

4. If substition reaction of octahedral complexes proceeds by dissociative mechanism via a square pyramid intermediate, stereochemistry of reaction products is retented. (i.e. *cis* gives 100% *cis* or *trans* gives 100% *trans*). If reaction proceeds by dissociative mechanism but via TBP intermediate, please discuss the stereochemistry of the products. (10%)

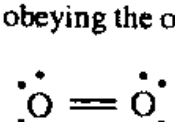
5. $Rh(PPh_3)_3Cl$ complex is an efficient catalyst as Wilkinson's catalyst for olefin hydrogenation. Please propose this catalytic cycle starting from CH_2=CHR. (12%)

6. What is ligand field theory ? What kind of properties can be obtained from this theory ? (10%).

7. What are the differences between molecular solids and solid state molecules ? (5%).

8. Why is DH_{vap} for water much greater than DH_{fus}? What does this reveal concerning changes in intermolecular forces in going from solid to liquid to vapor ? (5%)

9. A Lewis structure obeying the octet rule can be drawn for O_2 as follows:



Use the molecular orbital energy-level diagram for O_2 to show that this Lewis structure for O_2 corresponds to an excited state. (10%).

10. Using the p orbitals for an example, distinguish between the angular part of the probability function, the radial part of the probability function, and a probability contour. Draw simple sketches to illustrate. How could each of these be affected by a change in the principal quantum number, n ? (10%)

11. The Cope rearrangement is as follows:

carry out the appropriate symmetry analysis to show that it is thermally allowed. (10%).