

- (A) From the definition of electronegativity of atom by Mulliken,  $\chi \propto (I_A + E_A)$ , where  $I_A$  and  $E_A$  are ionization energy and electron affinity of atom A, respectively. Is it reasonable? (4%)

(B) Is the electronegativity of Carbon's C-H  $\sigma$  bond in  $C_2H_2$  greater or smaller than that in  $C_2H_6$ ? Why? (4%)
- Predict and explain the relation of CN stretching frequency of the following compounds:  $CN^-$ ,  $HCN$ ,  $SCN^-$ . (6%)
- Determine the point group of the following: (6%)
 

(a)  $NO_2^+$     (b)  $BrF_3$     (c)  $H_2C=C=CH_2$
- For the  $C_{2v}$  symmetry point group,
 

| $C_{2v}$ | E | $C_2$ | $\sigma_v(xz)$ | $\sigma_v(yz)$ |
|----------|---|-------|----------------|----------------|
| $A_1$    | 1 | 1     | 1              | 1              |
| $A_2$    | 1 | 1     | -1             | -1             |
| $B_1$    | 1 | -1    | 1              | -1             |
| $B_2$    | 1 | -1    | -1             | 1              |

(a) What are the symmetry of  $xy$  and  $R_x$ , respectively? (4%)

(b) What are the MO symmetry of the two O-H  $\sigma$  bonding in  $H_2O$ ? (6%)
- Give the approximate timescales of the following common structural techniques that can resolve a fluxional molecule. (5%)
 

(a) Nuclear magnetic resonance    (b) Infrared spectroscopy    (c) X-ray diffraction    (d) Mössbauer spectroscopy    (e) Chemical separation of isomers.
- Find organic fragments isolobal with each of the following: (6%)
 

(a)  $Fe(CO)_4$     (b)  $Fe(PR_3)_3$     (c)  $Cr(CO)_2$  ( $\eta^6-C_6H_6$ ).
- Draw the structures of the following: (8%)
 

(a)  $H_3PO_3$     (b)  $N_4S_4F_4$     (c)  $Fe_2(CO)_9$     (d)  $Ir_4(CO)_{12}$  ( $Ir(CO)_3$  is isolobal with P)
- Explain each of the following: (30%)
 

(a) The bond order of nitrogen oxide species is  $NO^+ > NO > NO^-$ .

(b) The conductivity of  $ICl$  is enhanced by adding  $AlCl_3$  or  $NaCl$ .

(c)  $(CH_3)_2O$  is a stronger base than  $(SiH_3)_2O$ .

(d) The vanadium-carbon distance in  $V(CO)_6$  is 200 pm, but only 193 pm in  $[V(CO)_6]^-$ .

(e) Two separate water exchange rates are found for  $Cu(H_2O)_6^{2+}$  in aqueous solution.

(f)  $[Cr(CN)_6]^{4-}$  is an inert complex while  $[Cr(H_2O)_6]^{2+}$  is labile.

9. Is the reaction  $[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  likely to proceed by an inner-sphere or outer-sphere mechanism? Explain your answer. (6%)
10. The anion  $[\text{Mn}(\text{CO})_5]^-$  reacts with 1,3-dibromopropane to form  $\text{Br}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Mn}(\text{CO})_5$ . However, the reaction does not stop there; the product reacts with additional  $[\text{Mn}(\text{CO})_5]^-$  to yield a carbene complex. Propose a structure for this complex, and suggest a mechanism for its formation. (8%)
11.  $[\text{Fe}(\text{CN})_6]^{3-}$  exhibits two sets of charge transfer absorptions, one of lower intensity in the visible region of the spectrum and one of higher intensity in the ultraviolet.  $[\text{Fe}(\text{CN})_6]^{4-}$ , however, shows only the high-intensity charge transfer in the ultraviolet. Explain. (7%)