

- Answer the following questions: (30%)
  - Which of the following mixtures would be expected to have maximum boiling points and which to have minimum boiling points? (a) Methyl acetate and chloroform, (b)  $C_6H_{12}$  and  $C_2H_5OH$
  - Which of the following complexes obey the rule of 18 (EAN rule)?
    - $Ni(NH_3)_6^{2+}$ ,  $Ni(CN)_4^{2-}$ ,  $Ni(CO)_4$
    - $Co(NH_3)_6^{3+}$ ,  $CoCl_4^{2-}$
  - Give the approximate pKa values for the following acids:
    - $H_3PO_3$ , (b)  $HNO_3$ , (c)  $HClO_4$
  - The Rate of reaction of  $O_2$  with  $trans-IrX(CO)(PPh_3)_2$  in benzene decreases in the order  $X = NO_2 > I > ONO_2 > Br > Cl > N_3 > F$ . Explain this observation.
  - Most substances expand when they are heated, leading to decrease density with increase temperature. However,  $H_2O(l)$  has a maximum density at  $4^\circ C$ . How can you explain this?
- Sketch  $\pi$  bonding orbitals that result from combination of the following orbitals on separate atoms:  $p_x$  and  $p_x$ ,  $p_x$  and  $d_{xz}$ ,  $d_{xz}$  and  $d_{xz}$ . (10%)
- Account for the difference in rate constants for the following two reactions: (10%)
  - $[Fe(H_2O)_6]^{2+} + Cl^- \rightarrow [Fe(H_2O)_5Cl]^+ + H_2O$   $k(M^{-1}sec^{-1}) = 10^6$
  - $[Ru(H_2O)_6]^{2+} + Cl^- \rightarrow [Ru(H_2O)_5Cl]^+ + H_2O$   $k(M^{-1}sec^{-1}) = 10^{-2.0}$
- Calculate the cation/anion radius ratio (by using plane geometry) for a triangular arrangement of anions in which the cation is in contact with the anions but does not push them apart. (10%)
- Would the following increase, decrease, or have no effect on the acidity? (10%)
  - Addition of  $SiO_2$  to molten  $Fe+FeO$ .
  - Addition of  $CuSO_4$  to  $(NH_4)_2SO_4$ .
- How might one distinguish between the following isomers? (15%)
  - $[Co(NH_3)_5Br]SO_4$  and  $[Co(NH_3)_5SO_4]Br$ .
  - $[Co(NH_3)_3(NO_2)_3]$  and  $[Co(NH_3)_6][Co(NO_2)_6]$ .
  - cis- and trans- $NH_4[Co(NO_2)_4(NH_3)_2]$ .
- Estimate the density of  $MgO$  (6PO) and  $ZnS$  (6PT) using radii to determine the cell dimensions and the number of formula units per unit cell. (15%)
 

Given: Mg:  $24.305 \text{ gmol}^{-1}$ , O:  $15.999 \text{ gmol}^{-1}$ , Zn:  $65.39 \text{ gmol}^{-1}$ , S:  $32.066 \text{ gmol}^{-1}$ .

Ionic radii (in  $\text{\AA}$ ) for Mg:  $0.49(4^+)$ ,  $0.72(6)$ ,  $0.89(8)$ ; O:  $1.35(2)$ ,  $1.38(4)$ ,  $1.40(6)$ ,  $1.42(8)$ ; S:  $1.7(6)$ ; : number in ( ) are the coordination number of the ion.