Inorganic Chemistry

Final Examination Jan.12, 2011

1. Draw the Lewis structure and give the point group of the following molecules (with highest possible symmetry.) (10%)
   (a) Sulfuric acid (b) Nitric acid (c) Phosphoric acid (d) Perchloric acid
   (e) Hydrazoic acid (HN_3)

2. Draw the 3-dimensional structure and give the point group of the following species. (10%)
   (a) Ferrocene (b) Diborane (c) $[Re_2Cl_8]^{2-}$ (d) S_8
   (e) $[K(18C6)]^+$ (in which, 18C6 = 18-Crown-6)

3. For each of the following reactions, identify the acid and the base. Also indicate which acid-base definition (Lewis, Solvent system, Bronsted-Lowry) applies. In some cases, more than one definition may apply. (10%)
   (a) $HClO_4 + CH_3CN \longrightarrow CH_3CNH^+ + ClO_4^-$
   (b) $PCl_5 + ICl \longrightarrow [PCl_4]^+ + [ICl_2]^-$
   (c) $2\ ClO_3^- + SO_2 \longrightarrow 2\ ClO_2 + SO_4^{2-}$
   (d) $2\ NOCl + Sn \longrightarrow SnCl_2 + 2\ NO$ (in N_2O_4 solvent)
   (e) $BH_4^- + 4\ H_2O \longrightarrow B(OH)_4^- + 4\ H_2$

4. Use Drago's E and C parameters(Table 1) to calculate ΔH for the reactions of pyridine and BF_3 and of pyridine and $B(CH_3)_3$. Repeat the calculations of the proceeding problem using NH_3 as the base, and put the four reactions in order of the magnitudes of their ΔH values. (6%)

Table 1 C_A, E_A, C_B, and E_B Values (kcal/mol)

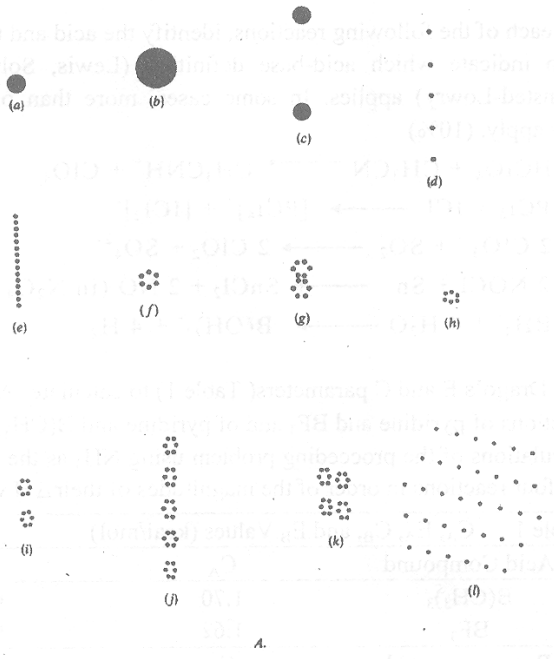
Acid Compound	C_A	E_A
$B(CH_3)_3$	1.70	6.14
BF_3	1.62	9.88
Base compound	C_B	E_B
Pyridine	6.40	1.17
NH_3	3.46	1.36

5. List the following acids in order of acid strength in aqueous solution (Hint: Use Pauling's equation): (6%)
   a. $HMnO_4$ H_3AsO_4 H_2SO_3 H_2SO_4
   b. HClO $HClO_4$ $HClO_2$ $HClO_3$

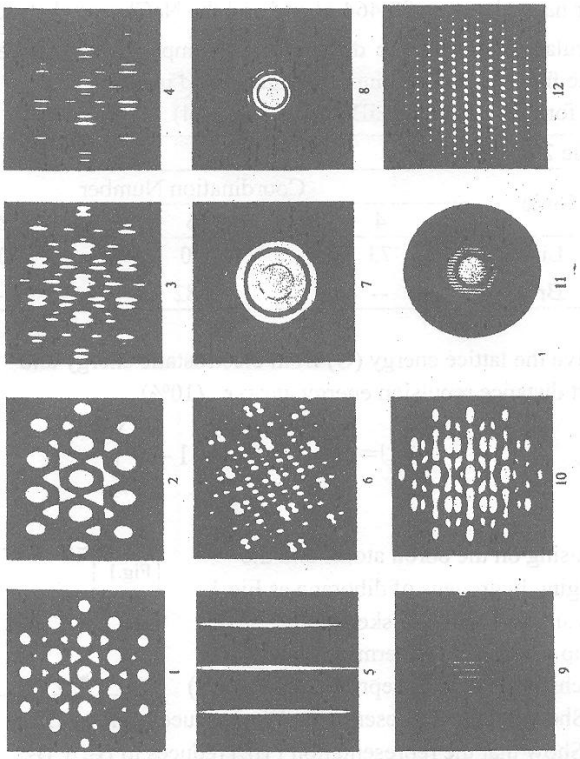
6. HF has $H_0 = -11.0$. Addition of 4% SbF_5 lowers H_0 to -21.0. Explain why this should be true, and why the resulting solution is so strongly acidic that it can protonate alkenes. (4%)

   $(CH_3)_2C{=}CH_2 + H^+ \longrightarrow (CH_3)_3C^+$

7. Diagram A shows some subjects and B shows some optical transforms. Match the objects to the transforms and determine their correct relative orientations. (12%)



A.



B

8. $F(hkl) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$

$$\rho(x,y,z) = \sum_h \sum_k \sum_l |F_{hkl}| \cdot e^{i\alpha}\, e^{-2\pi i(hx+ky+lz)}$$

Explain the meaning of each term in the two equations. (12%)

9. (a) Show that spheres occupy 74.0% of the total volume in a face-centered cubic structure in which all atoms are identical.
   (b) What percent of the total volume is occupied by spheres in a body-centered cube in which all atoms are identical.(8%)

10. LiBr has a density of 3.464 g/ cm^3 and the NaCl crystal structure. Calculate the interionic distance, and compare your answer with the value from the sum of the ionic radii found in Table 2. (6%)
(the fornula weight of LiBr is 86.85 g/mol)

Table 2 Ionic Radii

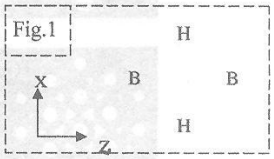
Ionic	Coordination Number		
	4	6	8
Li^+	73	90	106
Br^-	--	182	--

11. Derive the lattice energy (U) from electrostatic energy and short distance repulsion energy at $r = r_o$. (10%)

$$U = \frac{NMZ^+Z^-e^2}{r_o}\left(1 - \frac{1}{n}\right)$$

12. Focusing on the boron atoms and the bridging hydrogens of diborane as Fig.1, we can use Table 3 to sketch the group orbitals and determine their matching irreducible representations.(8%)

Fig.1



(a) Show that the representation $\Gamma(p_z)$ reduces to $A_g + B_{1u}$.
(b) Show that the representation $\Gamma(p_x)$ reduces to $B_{2g} + B_{3u}$.
(c) Show that the representation $\Gamma(1s)$ reduces to $A_g + B_{3u}$.
(d) Verify that the sketches for the group orbitals match their respective symmetry designations (A_g, B_{2g}, B_{1u}, B_{3u}) in Table 3. (Please use the fill-in-the-blank form of Table 4 to answer (d))

Table 3 Character Table

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x
A_u	1	1	1	1	−1	−1	−1	−1	
B_{1u}	1	1	−1	−1	−1	−1	1	1	z
B_{2u}	1	−1	1	−1	−1	1	−1	1	y
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

Table 4	designations	Group Orbitals Sketches
p_z	A_g	
	B_{1u}	
p_x	B_{2g}	
	B_{3u}	
s	A_g	
	B_{3u}	

13. The reaction $P_4(g) \rightleftharpoons 2\,P_2(g)$ has $\Delta H = 217$ kJ/ mol. If the bond energy of a single phosphorous-phosphorous bond is 200 kJ/mol, calculate the bond energy of the P≡P bond. Compare the value you obtain with the bond energy in N_2 (946 kJ/ mol), and suggest an explanation for the difference in bond energies in P_2 and N_2.(6%)

14. BrF_3 undergoes autodissociation according to the equilibrium

$$2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

ionic fluorides such as KF behave as base in BrF_3, whereas some covalent fluorides such as SbF_5 behave as acids. On the basis of the solvent system concept, write balanced chemical equations for these acid-base reactions of fluorides with BrF_3.(4%)

15. Give the name ***in English***, indicate their magnetic properties (paramagnetic, diamagnetic) and rationalize the bond distance.(12%)

Table 5 Neutral and Ionic O_2 and O_3 Species			
Formula	Name	Magnetic Property	O-O Distance (pm)
O_2^+	oxidonium		111.6
O_2	oxygen		120.8
O_2^-	oxygenion		135
O_2^{2-}	peroxy		149
O_3	ozone		127.8
O_3^-	ozonium		134

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