

Chapter 5, problem

5.11

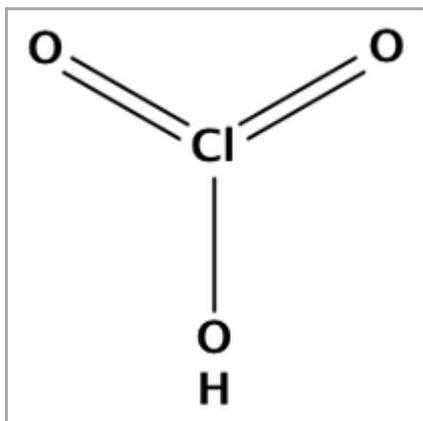
The strength of aqua acids typically increases with increasing positive charge of metal ion and with decreasing ionic radius. Therefore, the strength of aqua acids of Sr^{2+} and Ba^{2+} , both in alkaline earth group, is $\text{Sr}^{2+} > \text{Ba}^{2+}$ according to the variation in the radius. As to Hg^{2+} , which has pseudo-noble electron configuration, is a highly polarizing ion. The Hg-O bond is rather covalent and strong. As a result, the HgO-H bond is easy to dissociate and the strength of aqua acid of Hg^{2+} is the most strongest among the three divalent cations. The Bronsted acidities vary in $\text{Hg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

References:

1. textbook, p151.
2. <http://www.ktf-split.hr/periodni/en/abc/kpt.html>

5.12

Chloric acid, HClO_3 , is an oxoacid of chlorine. It is a strong acid ($\text{pK}_a \sim -1$) and oxidising agent. The structure of HClO_3 is pyramidal as shown in following.



Chlorous acid, HClO_2 , is unstable and its pK_a is ca. 7.6.

The structure is shown in the following.



Pauling's rule: $\text{pK}_a = 8 - 5p @ 25^\circ\text{C}$, where p is the number of oxo groups ($\text{M}=\text{O}$) per molecule.

HClO_3 can be written as $\text{O}_2\text{Cl}(\text{OH})$, and the pK_a predicted by Pauling's rule is $8 - 5 \times 2 = -2$.

HClO_2 can be written as $\text{O}_1\text{Cl}(\text{OH})$, and the pK_a predicted by Pauling's rule is $8 - 5 \times 1 = 3$.

Because each oxo group is highly electronegative, it draws electrons away from the central atom and increases the positive charge on the center atom. This positive charge in turn draws the electrons of the hydrogenated oxygen toward itself. The net result is a weaker O-H bond, which makes it easy for the molecule to act as an acid by losing the H^+ . As the number of highly electronegative oxygens increases, the acid strength of the molecule also increases.

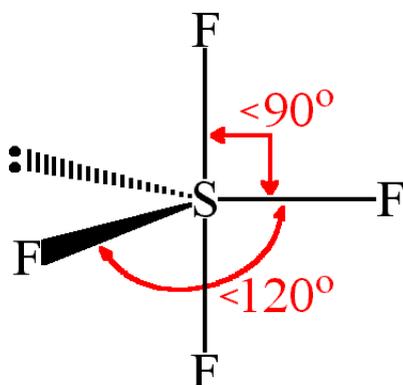
References:

1. http://en.wikipedia.org/wiki/Chloric_acid
2. textbook, p152-153.

5.13

SO_3 is a planar molecule and SO_2 is a bent molecule. Both react with pyridine without any steric hindrance. The high oxidation state of S on SO_3 makes it form stronger Lewis acid-base complex with pyridine than SO_2 .

SF_4 has a see-saw structure, and SF_6 has an octahedral molecular structure. Pyridine forms a weak complex with SF_6 because of the steric hindrance.



5.14

(a) CdI_2 , where Cd^{2+} is soft ion and I^- is soft. CaF_2 , where Ca^{2+} is hard ion and F^- is hard ion. Thus, the equilibrium constant is less than 1.

(b) CuI_4^{2-} , where Cu^{2+} is hard ion and I^- is soft ion. $CuCl_4^{3-}$, where Cu^+ is soft and Cl^- is hard ion. Thus, the equilibrium constant is greater than 1.

(c) The basicity of NH_2^- is stronger than OH^- . Therefore, the equilibrium constant is greater than 1.