Inorganic Chemistry with Doc M.

Fall Semester, 2012

Day 10. Acids and Bases Overview

Name(s):	**Element:**

Topics:

1. Bronsted-Lowry Concept
2. Lewis acid and base concepts
3. Oxyacids
4. Polyprotic acids
5. pH of salts
6. Hard-soft acid and base theory
7. Oxides

1. Bronsted-Lowry concepts

The most significant improvement of B-L over Arrhenius is the concept of acid and conjugate base and the relationship between them: $K_a \times K_b = K_w$. (a) Write the equilibrium expression for nitrous acid, HNO_2, a weak acid. Write the equilibrium expression for the conjugate base of nitrous acid, nitrite, NO_2^-, a weak base. Add the two equilibria together and show how $K_a \times K_b = K_w$.

(b) Complete this table of acid/base conjugate pairs.

Acid	K_a	Base	K_b
chromic acid, H_2CrO_4	1.8×10^{-1}		
hydrofluoric acid, HF	3.5×10^{-4}		
phosphoric acid, H_3PO_4	7.5×10^{-3}		
dihydrogen phosphate, $H_2PO_4^-$	6.2×10^{-8}		
hydrogen phosphate, HPO_4^{-2}	4.8×10^{-13}		
		lead(II) hydroxide, $Pb(OH)_2$	9.6×10^{-4}
		ammonia, NH_3	1.8×10^{-5}
		methyl amine, CH_3NH_2	3.7×10^{-4}

2. Lewis acid and base concepts

Which of these species could be Lewis acids? Circle them. Which could be Lewis bases? Draw a box around them.

NH_3	BF_3	Al^{+3}	CH_4	CPh_3^{+} (Ph = C_6H_5)
H_2O	F^-	Cl^-	Fe^{+2}	$AlCl_3$

3. Oxyacids

Know that the acid strength generally increases with the oxidation number (or you can look at it as with the number of oxygen atoms) in the series, HXO_n. An easy to remember explanation is based on the stability of the anion: strong acids must have stable conjugate bases and the extra oxygens help carry the charge of the anion.

Acid	K_a	pK_a
HClO	3.5×10^{-8}	7.5
$HClO_2$	1.2×10^{-2}	1.9
$HClO_3$	approx 1	0
$HClO_4$	very large	-

Acid	K_a	pK_a
H_3AsO_3	6×10^{-10}	9.23
H_3AsO_4	5.6×10^{-3}	2.25

Acid	K_a	pK_a
HSO_3^-	1.0×10^{-7}	6.91
HSO_4^-	1.2×10^{-2}	1.92

Rank these acids from strongest acid to weakest acid

HIO, HIO_2, HIO_3, HIO_4
$NaHSeO_3$, $NaHSeO_4$

4. Polyprotic acids

For polyprotic acids, the change in pK_a is between 3 – 5 for each subsequent proton lost.

Acid	K_a	pK_a
H_3PO_4	7.5×10^{-3}	2.12
$H_2PO_4^-$	6.2×10^{-8}	7.21
HPO_4^{-2}	4.8×10^{-13}	12.31

Acid	K_a	pK_a
H_3AsO_4	5.6×10^{-3}	2.25
$H_2AsO_4^-$	1.7×10^{-7}	6.77
$HAsO_4^{-2}$	4.0×10^{-12}	11.60

Estimate pK_a and K_a for the second proton lost for germanic acid:

Acid	K_a	pK_a
H_2GeO_3	2.6×10^{-9}	8.59
$HGeO_3^-$		

5. pH of salts

A. Know that anions of the strong monoprotic acids (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) are pH neutral (7) and the cations of the strong bases (Li^+, Na^+, K^+, Rb^+, and Cs^+) are pH neutral.

B. The anions of monoprotic weak acids are weak bases. For weak bases, the protonated conjugate acid is always a weak acid. Predict the acid-base nature of each of these salts (< 7, = 7, > 7)

LiCl
KBr
NH_4NO_3
$RbNO_2$
CsF
$Fe(ClO_4)_2$
$NaHSO_4$
Na_2SO_4
$NaC_2H_3O_2$

6. Hard-soft acid-bases chemistry.

Hard acids are small and capable of polarizing electron clouds of bases: Li^+, Na^+, K^+, Be^{+2}, Mg^{+2}, Ca^{+2} Sr^{+2}, Al^{+3}, Cr^{+3}

Soft acids are larger and not as able to polarize electron clouds on bases: Tl^+, Cu^+, Ag^+, Au^+, Hg_2^{+2}, Hg^{+2}, Pd^{+2}

Hard bases are small and not very polarizable: F^-, Cl^-, H_2O, OH^-, NO_3^-, NH_3, SO_4^{-2}, ClO_4^-

Soft bases are larger and more easily polarized: I^-, H_2S, HS^-, S^{-2}, SCN^-, CN^-, PR_3, AsR_3

Hard-hard combinations are generally ionic in nature and have large lattice energies, thus making them less soluble than hard-soft or soft-hard interactions. Soft-soft compounds have a fair amount of covalent character and are also less soluble than hard-soft or soft-hard interactions. One can even predict the direction of an equilibrium based on driving towards the favored hard-hard or soft-soft compounds.

$$CuCl + NaCN \xrightarrow{\longleftarrow} CuCN + NaCl$$

Predict the direction of the equilibrium for each of the following:

LiF + AgI [ ] LiI + AgF
2 KSCN + $Hg(NO_3)_2$ [ ] 2 KNO_2 + $Hg(SCN)_2$
$FeSCN^+$ + $PtCl_4^{-2}$ [ ] $FeCl_4^{-2}$ + $PtSCN^+$

I. Non-aqueous solvents. Back when you were pups, you learned that there were six strong acids. Write their formulas here:

What makes an acid a "strong acid"? Use an example.

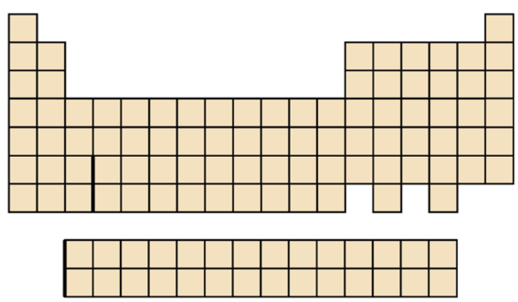
There are, however, dozens of strong acids, including acids such as HSO_3F and HSO_3CF_3. Those that are stronger than sulfuric acid are called ***super acids***. It is actually possible to differentiate the relative order of acid strength; we just can't do it in water where these strong acids protonate water 100%. Instead we must use a solvent that is more difficult to protonate. Glacial acetic acid (pure 100% acetic acid with no water), is such a solvent (and there are many others). Glacial acetic acid is a liquid at room temperature and has a boiling point of 118 ^oC. Another solvent that can be used is pure sulfuric acid. Write the autodissociation for water, acetic acid and sulfuric acid, each as pure solvents.

Write the equilibrium that would occur when HCl and HBr were added to glacial acetic acid in order to determine which of the two were the strongest.

7. Oxides.

Oxides as a periodic trend. Write the reaction that occurs when sodium oxide reacts with water. Repeat for calcium oxide. This is a typical reaction between an alkali metal oxide or an alkaline earth oxide and water. These oxides are frequently called ***base anhydrides***.

Beryllium oxide, interestingly is not a basic oxide. We will discuss it below. However, indium(III) oxide and thallium(III) oxide are also basic oxides. Shade them in on the periodic table.



Write the reaction that occurs when sulfur trioxide reacts with water. This is a typical reaction between non-metal oxides and water. These oxides are frequently called ***acid anhydrides***.

Acidic oxides. Acid anhydrides are part of a larger class of compounds called ***acidic oxides***. The acidic oxides include Be_2O_3, CO_2, SiO_2, GeO_2, N_2O_5, P_4O_{10}, As_2O_5, Sb_2O_5, Bi_2O_5, SO_2, SO_3, SeO_2, SeO_3, TeO_2, TeO_3, Cl_2O_5, Cl_2O_7, Br_2O_5, I_2O_5, amongst others. Draw a box around these elements on the periodic table. Some of these are acid anhydrides, meaning they react with water to form acids. Sulfur trioxide was such an example. Others do not react with water, but do react with bases. Acidic oxides do not react with acids. Silicon dioxide is an example of an acidic oxide that does not react with water, but does react with bases. Write and balance the equation for the reaction between silicon dioxide and hydroxide to produce silicon $SiO_2(OH)_2^{-2}$.

Amphoteric oxides. Some oxides are amphoteric. That is, they react with both acids and bases. Amphoteric oxides include BeO, Al_2O_3, Ga_2O_3, SnO_2, and PbO_2. Indicate them on the periodic table.

Let's pursue how aluminum oxide reacts with both acids and bases. Write and balance the reaction that occurs when aluminum oxide reacts with H^+ to produce Al^{+3}(aq).

Write and balance the reaction that occurs when aluminum oxide reacts with OH^- to produce $Al(OH)_4^-$ (aq). (Balance it like a redox reaction, adding waters if needed, etc.)

Review for the ACS Final Exam: Acids and bases, amphoterism

1. Rank these compounds from most acidic to least acidic:
   (a) $NH_3 > H_2O > NaNH_2$
   (b) $H_2O > NH_3 > NaNH_2$
   (c) $NH_3 > NaNH_2 > H_2O$
   (d) $H_2O > NH_3 > NaNH_2$
   (e) None of these are acids

2. Which of these is not a Lewis base?
   (a) H_2O
   (b) PF_3
   (c) NH_3
   (d) OH^-
   (e) SO_3

3. What is the strongest acid that can exist in glacial acetic acid?
   (a) H_3O^+
   (b) $H_2C_2H_3O_2^+$
   (c) $C_2H_3O_2^-$
   (d) H_2O
   (e) H_2SO_4

4. Which of the following is not an acid anhydride?
   (a) P_4O_{10}
   (b) SO_3
   (c) N_2O_5
   (d) CO_2
   (e) $HClO_4$

5. Which of the following is the best solvent to differentiate the acid strengths of HCl and HBr?
   (a) CH_3CN
   (b) H_2O
   (c) NH_3
   (d) CH_3COOH
   (e) CCl_4

6. Which of the following is not a Brönsted acid in water?
   (a) $HClO_4$
   (b) $NaNO_3$
   (c) HCl
   (d) HNO_2
   (e) CH_3COOH

7. In which case would the equilibrium be expected to lie to the right?
   (a) $MgF_2 + HgI_2 \rightleftarrows MgI_2 + HgF_2$
   (b) $AgBr + NaCl \rightleftarrows AgCl + NaBr$
   (c) $Hg_2I_2 + MgF_2 \rightleftarrows Hg_2F_2 + MgI_2$
   (d) $CuO + 2\ Cu_2S \rightleftarrows CuS + 2\ Cu_2O$
   (e) $CdCl_2 + K_2S \rightleftarrows CdS + 2\ KCl$

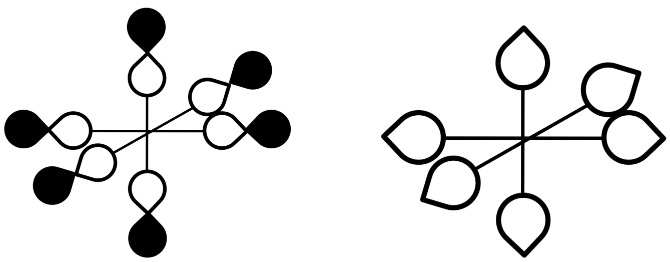
8. The chemical nature of an element's oxide is a predictable trend. Which of these oxides is most likely amphotertic?
   (a) SO_3
   (b) CaO
   (c) CrO_3
   (d) K_2O
   (e) Ga_2O_3

9. Which of the following compounds would have the largest percent ionic character?
   (a) BeO
   (b) KCl
   (c) CsF
   (d) LiI
   (e) RbI

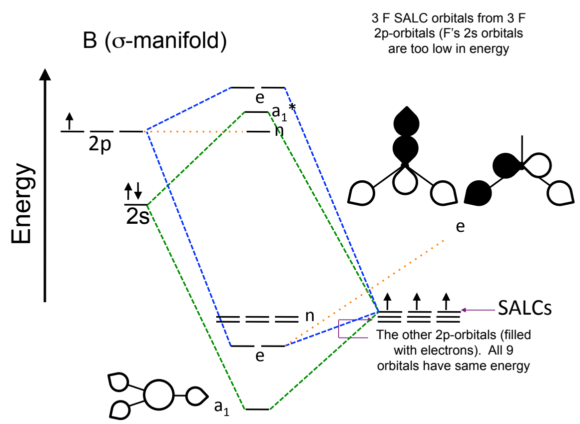
***Answers**: B, E, B, E, D, B, E, E, C*

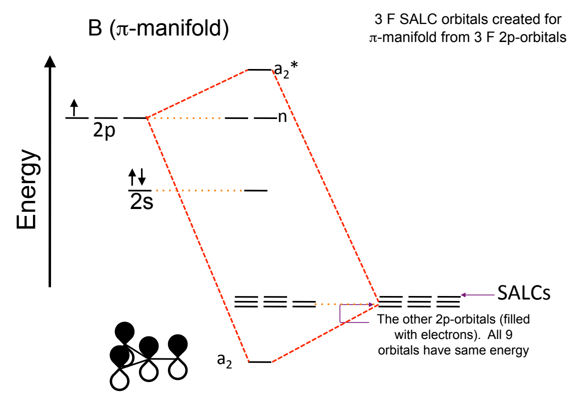
Answers to Day 9:

SF_6

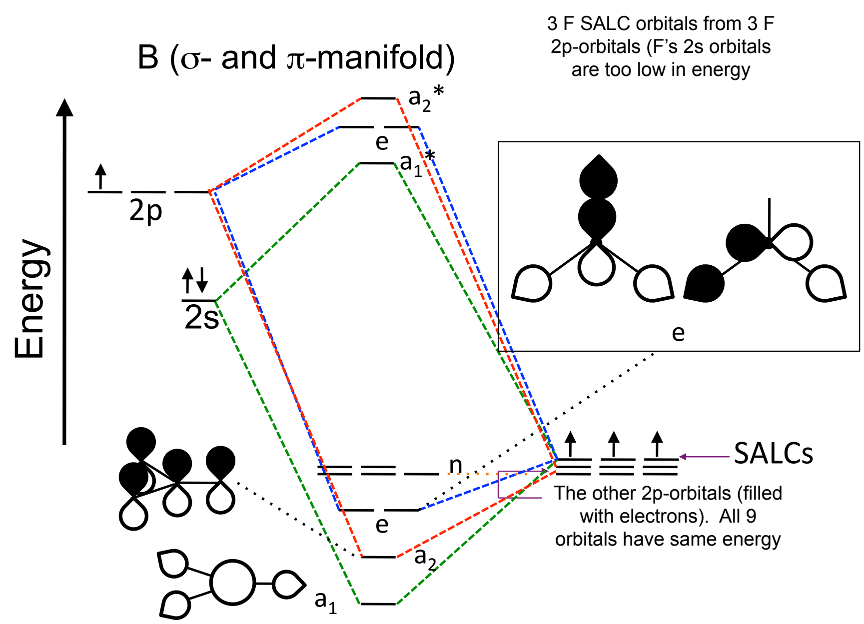


2. σ-bonding in BF_3 and π-bonding in BF_3

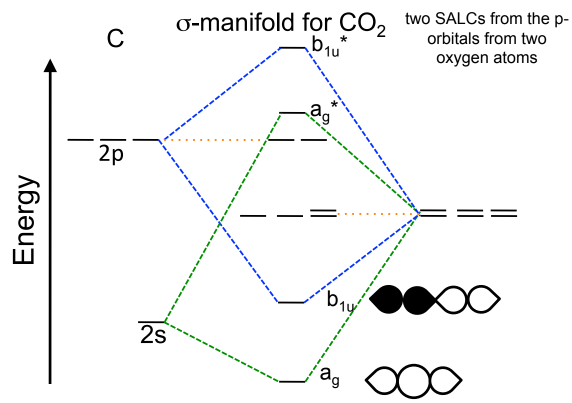


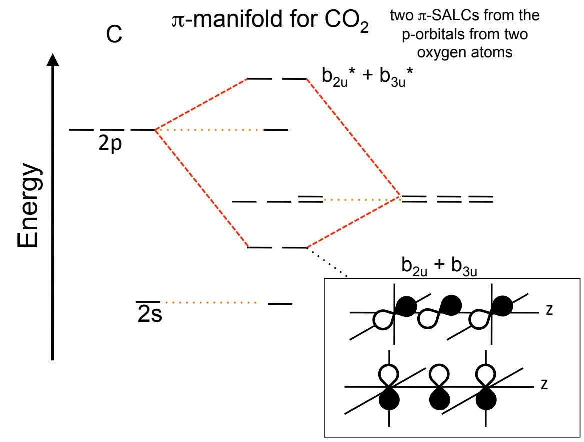


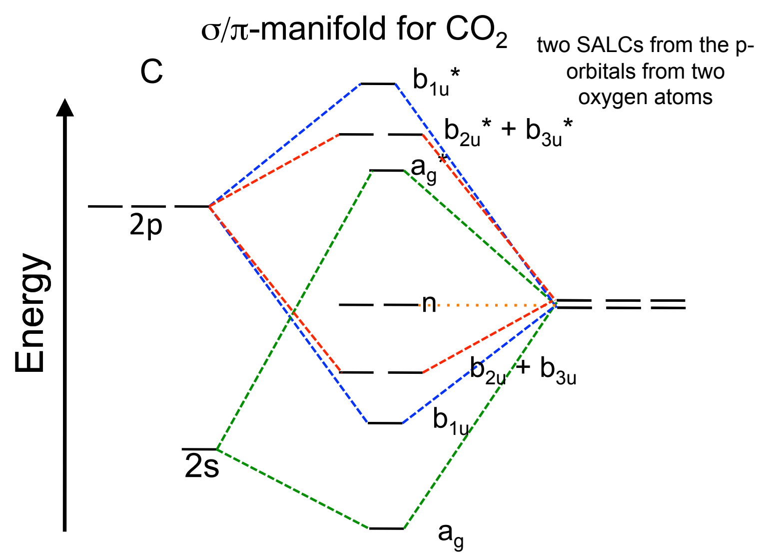
2. Combined σ-bonding and π-bonding in BF_3



3. σ-bonding in CO_2 and π-bonding in CO_2







	E	C_2	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	
Γ	2	-2	0	0	0	0	-2	2	
B_{2u}	1	-1	1	-1	-1	1	-1	1	p_y
B_{3g}	1	-1	-1	1	1	-1	-1	1	

For the p_x orbitals:

	E	C_2	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	
Γ	2	-2	0	0	0	0	2	-2	
B_{3u}	1	-1	-1	1	-1	1	1	-1	p_x
B_{2g}	1	-1	1	-1	1	-1	1	-1	