GHW # 6

CHEM 2811(01) Winter 2014. CHAPTER 4. Name: Whitney Major (Feb 20, 2014)

1. Figure out the driving force for following reactions. [formation of insoluable salt that pull out from the solution]

a) $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$ (Arrhenius) — B, A, salt, water — formation of H_2O (water)

b) $Na_2CO_3 + 2HCl \rightarrow H_2O + CO_2(g) + 2NaCl$ — salt, A, water, g, salt — formation of gas (CO_2)

c) $NH_4Cl + NaOH \rightarrow NH_3(g) + H_2O + NaCl$ — salt, B, gas, water, salt — formation of gas (NH_3)

d) $Na_2SO_4 + Pb(NO_3)_2 \rightarrow PbSO_{4(s)} + 2NaNO_3$ — salt 1, salt 2, salt 3 insoluable, salt 4 — salt-salt precipitation (double displacement) formation of insoluable salt ($PbSO_4$) (solid)

e) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$ — metal, acid, salt, element — single displacement (redox) formation of redox $E_{cell} = +$

2. Identify the conjugate acid/base pairs in following reactions. [Bronsted/Lowery]

a) $HF(aq) + H_2O \rightarrow H_3O^+(aq) + F^-(aq)$ — acid 1, base 1, acid 2, base 2 (ion) — $HF \rightarrow F^-$ (acid, conj base ion); $H_2O \rightarrow H_3O^+$ (base, conj acid)

b) $H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$ — acid 1, base 1, base 2, acid 2 — $H_2O \rightarrow OH^-$ (acid (wk), conj base (stronger)); $NH_3 \rightarrow NH_4^+$ (base (wk), conj acid (stronger))

c) $H_2Fe(CO)_4 + CH_3OH \rightarrow [FeH(CO)_4]^- + CH_3OH_2^+$ — acid, base, base, acid — $H_2Fe(CO_4) \rightarrow [FeH(CO)_4]^-$ (acid, conj base); $CH_3OH \rightarrow CH_3OH_2^+$ (base, conj acid)

d) $NH_3 + H_2S \rightarrow NH_4^+ + HS^-$ — base, acid, acid, base — $NH_3 \rightarrow NH_4^+$ (base, conj acid); $H_2S \rightarrow HS^-$ (acid, conj base)

3. Identify the conjugate bases corresponding to the following acids:,

(a) $[Co(NH_3)_5(OH_2)]^{+3} \rightarrow [Co(NH_3)_5(OH)]^{2+}$

(b) $HSO_4^- \rightarrow SO_4^{2-}$

(c) $CH_3OH \rightarrow CH_3O^-$

(d) $H_2PO_4^- \rightarrow HPO_4^{2-}$

(e) $Si(OH)_4 \rightarrow [Si(OH)_3O]^{-1}$

(f) $HS^- \rightarrow S^{2-}$

(g) $[Fe(OH_2)_6]^{2+} \rightarrow [Fe(OH)_5O]^{+1}$

[aqua acids - acid coming fr H_2O molecule]

4. For each of the following processes, identify the acids and bases involved and characterize the process as complex formation or acid–base displacement. Identify the species that exhibit Brønsted acidity as well as Lewis acidity.

a) $SO_3 + H_2O \rightarrow HSO_4^- + H^+$ — LA, LB — Lewis acid/base reaction

b) $CH_3[B_{12}] + Hg^{2+} \rightarrow [B_{12}]^+ + CH_3Hg^+$ (B_{12} designates the cobalt macrocycle vitamin B_{12}) — (soft acid) — transfered to Mercury — displacement reaction — CH_3^- hard base — Hg^{2+} - harder acid — porphyrin (hemoglobin) no clear e^- donor/acce

c) $KCl + SnCl_2 \rightarrow K^+ + [SnCl_3]^-$ — more stable complex — Cl ion transfer — Cl & $SnCl_2$ (softer) bonds formation — Lewis acid/base formation

d) $AsF_3(g) + SbF_5(l) \rightarrow [AsF_2]^+[SbF_6]^-(s)$ — LA, LB — complex ion

5. A acid HB is dissociating according to the following equation in water.

$HB(aq) \leftarrow H^+(aq) + B^-(aq)$ $\quad HB + H_2O \rightleftharpoons H_3O^+ + B^-$ $\quad K_a = \frac{[H_3O^+][B^-]}{[HB]}$

(s) (l) liq H_2O doesn't appear in eq rxn

A solution of HB was prepared by dissolving 1.00 mol of HB in 1 liter of water. After the equilibrium is established HB was found to be 20% dissociated. Calculate K_a and pK_a for the acid HB.

	HB	+ H_2O ⇌	B^-	+ H_3O^+
I	1		0	0
C	-x		x	x
E	1-x		x	x
	=0.8		=0.2	=0.2

1 mole
20% = 0.2
80% = left over

$K_a = \frac{(0.2)^2}{0.8} = 0.05$ $\quad K_a = \frac{x^2}{M-x}$ drop x for wk acid $\quad x = \sqrt{K_a M}$

$pK_a = -\log K_a = -\log(0.05) = 1.30$

calc pOH
$14 - pH = pOH$

6. **Arrange the following compounds in order of increasing acidity:**

HI (pK_a = -11), H_2CO_3 (pK_a = 6.37), H_2SO_3 (pK_a = 1.81), HCN (pK_a = 9.31)

HCN < H_2CO_3 < H_2SO_3 < HI

lower pKa = stronger acid

7. **Explain the trend shown by following binary acids in water:**

	HF	HCl	HBr	HI
pK_a	+3	-7	-9	-11

	NH_3	H_2O	HF
pK_a	+33	+14	+3

↓ pka value. HF weaker than HI; bond energy in H-I; bond dissociation (larger atom)

8. **Which acids of the following pairs of acids is the stronger acid?**

a) $[Fe(OH_2)_6]^{3+}/[Fe(OH_2)_6]^{2+}$ — aqua acids (hexaaqua 3+) (hexaaqua Fe^{2+}); $[Fe(OH_2)_6]^{3+}$ - stronger

b) $Al(OH_2)_6^{3+}/Ga(OH_2)_6^{3+}$ — aqua acids. Al smaller than Ga; EN of Al > EN Ga; $Al(OH_2)_6^{3+}$ more acidic

c) $Si(OH)_4/Ge(OH)_4$ — aqua acids; $Si(OH)_4$ more acidic

d) $HClO_3/HClO_4$ — oxy acids; $HClO_4$ more acidic

e) $H_2CrO_4/HMnO_4$ — oxy acids; $HMnO_4$ more acidic

f) H_3PO_4/H_2SO_4 — H_2SO_4 more acidic

g) H_2SO_4/H_2SeO_4 — H_2SO_4 more acidic

h) $HIO_4/HClO_4$ — Cl smaller higher electronegativity (pull of e^- in bond); $HClO_4$ - stronger acid

higher ON or charge more acidic

9. **Which of the following elements form oxide polyanions and which forms oxide polycations?**
Al, As, Cu, Mo, Si, B, Ti

Al, Cu, Ti - cation; As, Mo, Si, B - anion (also P)

polyanions & poly cations are chemical species containing more than one charged particle

10. **Identify the Lewis acids and bases in following reactions:**

a) $BrF_3 + F^-$ ---> BF_4^- — Lewis A/B adduct; $K_f = \frac{[BrF_3][F^-]}{[BF_4^-]}$ higher means stronger

b) $BF_3 + NH_3$ ---> $F_3B\text{-}NH_3$ — B - electron difficiency; NH_3 e^-; LA - lone pair acceptor

c) $FeCl_3 + Cl^-$ --> $FeCl_4^-$

d) $I^- + I_2$ --> I_3^-

e) $(SnCl_3)^- + (CO)_5MnCl$ ---> $(CO)_5Mn\text{-}SnCl_3 + Cl^-$ — $K_{f_1} < K_{f_2}$; soft → kicks out harder Cl^-

The aqua ions of metals that have amphoteric oxides generally undergo polymerization to polycations. The elements Al, Cu, Ti fall into this category. Polyoxoanions are important for d-block metals, especially Mo.

11. **Explain why Na^+ prefers F^- to I^- where as Cu^+ prefers I^- to F^-.**

$Na^+ + F^- \rightarrow NaF$; $Cu^+ + I^- \rightarrow CuI$. Cu^+ ionic radius is larger than Na^+ and I^- ionic radius is larger than F^-. F^- is a harder base and I^- is a softer base. Na^+ a harder acid, Cu^+ is a softer acid.

12. **Consider the Lewis acids $(CH_3)_3Al$ and $(CH_3)_3Ga$ and the Lewis bases $(CH_3)_3N$, $(CH_3)_3P$, and $(CH_3)_3As$.**

$(CH_3)_3Al$ will react most favorably with $(CH_3)_3N$ (hard acid, hard base, electron deficient)

$(CH_3)_3Ga$ will react most favorably with $(CH_3)_3P$. (soft acid, soft base) $As(CH_3)_3$ [softer base than P]

NaF has a higher K_F value > K_F value of NaI; stronger ionic bond formation. K_F CuI larger > K_F CuF smaller; density lower; both are weak bond formation

13. **Explain the reaction sequence given below in terms of hard and soft Lewis acid-base behavior:**

R_3SiNC ---- AgCl ---- R_3SiCl ---- AgF ---- R_3SiF

hard - predom having e^- [ ] of inert gases; borderline - intermediate; soft - e^- [ ] in outer shell similar to Ni^o, Pb^o, Pt^o

14. **Explain why HF acid is used to make marks and dissolve glass.**

because it breaks the Silicon bonds. HF - hard acid - dissolve outer layer

15. **Which of the following metal expected to be found in alumino silicate minerals and which in sulfides? Cd, Rb, Cr, Pb, Sr, Pd**

amino silicate minerals = hard acids; sulfides = soft acids

$CuS + O_2 \xrightarrow{\Delta} SO_2 + Cu$; AuS - gold not reactive

Cd, Pb, Pd - softer acids

Rb, Cr, Sr - harder acids

$F = \frac{q^2}{r}$; sm cation, lg anion; perferably NaF over NaI & CuI over CuF.

$Na^+(aq) + F^-(aq) \rightarrow NaF$; $K_F = \frac{[NaF]}{[Na^+][F^-]}$