**Homework set #1 CHEM 311**

6-A

(1) $Ag^+ + Cl^- \Leftrightarrow AgCl(aq)$
(2) $AgCl(aq) + Cl^- \Leftrightarrow AgCl_2^-$
(3) $AgCl(s) \Leftrightarrow Ag^+ + Cl^-$

a)

add equations 1 and 3 to get

(4) $AgCl(s) \Leftrightarrow AgCl(aq)$, so $K_4 = K_1 * K_3 = 3.6*10^{-7}$

b) $K_4 = [AgCl(aq)] = 3.6*10^{-7}$ M

c)

flip equation (2)
(5) $AgCl_2^- \Leftrightarrow AgCl(aq) + Cl^-$ $(K_5=1/K_2)$

flip equation (4)
(6) $AgCl(aq) \Leftrightarrow AgCl(s)$ $(K_6 = 1/K_4)$

add equations (5) and (6) to get
(7) $AgCl_2^- \Leftrightarrow AgCl(s) + Cl^-(aq)$,
so $K_7 = K_5K_6 = 1/(K_2K_4) = 1/(K_1K_2K_3) = 3.0*10^4$ M

**6B**

a) $K = [H^+]^8[Br^-][Cr_2O_7^{2-}]/[BrO_3^-][Cr^{3+}]^2$
$K = \{(1+8x)^8(x)(x)\} / \{(0.0100-x)(0.0100-2x)^2\}$

b) $1x10^{11} = (1.04)^8(0.0050)^2 / (.0050)([Cr^{3+}]^2)$
$[Cr^{3+}] = \{((1.04)^8(0.0050)^2) / (.0050)(1x10^{11})\}^{1/2}$
$= 2 \cdot 10^{-7}$ M

**6D**

a) $Ca(IO_3)_2$

$Ksp = [Ca^{+2}][IO_3^-]^2$

If the $Ca(IO_3)_2$ is the only source of $Ca^{+2}$ and $IO_3^-$ in solution, than $[IO_3^-] = 2[Ca^{+2}]$

$Ksp = [Ca^{+2}](2[Ca^{+2}])^2 = 4[Ca^{+2}]^3 = 7.1*10^{-7}$

$[Ca^{+2}] = 5.6*10^{-3}$ M

$5.6*10^{-3}$ mol $Ca(IO_3)_2$ dissolve per Liter

$Ba(IO_3)_2$

$Ksp = [Ba^{+2}][IO_3^-]^2$

If the $Ba(IO_3)_2$ is the only source of $Ba^{+2}$ and $IO_3^-$ in solution, than $[IO_3^-] = 2[Ba^{+2}]$

$Ksp = [Ba^{+2}](2[Ba^{+2}])^2 = 4[Ba^{+2}]^3 = 1.5*10^{-9}$

$[Ba^{+2}] = 7.2*10^{-4}$ M

$7.2*10^{-4}$ mol $Ba(IO_3)_2$ dissolve per Liter

$Ca(IO_3)_2$ is more soluble

b) $Ca(NO_3)_2$

**6H**

a) neutral

b) $CH_3CO_2^-$ is the conjugate base of acetic acid, $CH_3CO_2H$, (basic)

c) $NH_4^+$ is the conjugate acid of ammonia $NH_3$, (acidic)

d) $PO_4^{-3}$ is a weak base, (basic)

e) neutral, $(CH_3)_4N^+$ can not accept or donate a proton in water

f) $C_6H_5CO_2^-$ is the conjugate base of benzoic acid (basic)

g) $Fe^{3+}$ is a Lewis acid (acidic)

**6-3** It is possible that thermodynamically favored reactions happen to slowly that the reactants appear to be stable. For example, $^{87}$Rb decays to $^{87}$Sr with a half-life of over a billion years. Thus, the ratio of $^{87}$Rb / $^{87}$Sr measured today will be about the same as the ratio measure a year from now, but the reaction is thermodynamically favorable.

**6-4**

a) $3Ag^+(aq) + PO_4^{3-}(aq) \leftrightarrow Ag_3PO_4(s)$

$$K = 1 / ([Ag^+]^3[PO_4^{3-}])$$

b) $C_6H_6(l) + 15/2O_2(g) \leftrightarrow 3H_2O(l) + 6CO_2(g)$

$$K = P_{CO2}^{\ 6} / P_{O2}^{\ 15/2}$$

$C_6H_6$ and water do not go into the equilibrium expression because it is not in a dilute solution. It is in its pure form, and so its concentration is its density, which is a constant. All constants are grouped into the equilibrium constant. The gases are written in terms of pressures, and the values for these are substituted with the units of atmospheres.

**6.6**

| | |
|---|---|
| $HOCl \leftrightarrow H^+ + OCl^-$ | $K_1 = 3.0*10^{-8}$ |
| $HOCl + OBr^- \leftrightarrow HOBr + OCl^-$ | $K_2 = 15$ |

What is the K for the following reaction?

$HOBr \leftrightarrow H^+ + OBr^-$

Set up the above equations such that when you add them together they yield the equation where looking for.

| | | |
|---|---|---|
| | $HOCl \leftrightarrow H^+ + OCl^-$ | $K_1 = 3.0*10^{-8}$ |
| + | $OCl^- + HOBr \leftrightarrow OBr^- + HOCl$ | $K_{-2} = 1/15$ |
| (1 pt) | | (1 pt) |
| | $HOBr \leftrightarrow H^+ + OBr^-$ | $K = K_1*K_{-2} = 2.0*10^{-9}$ |

**6-9**

a) right

b) neither

c) right

d) larger

**6-10**

a) $K = p_{H2O}$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta G^0 = 63.11 - 298*(.148) = 19.10$ kJ/mol

$Kp = e^{-\Delta G0/RT} = e-(19100/(8.314*298)) = 0.000391$ bar

b)

1 bar = 0.9869 atm, this is very close to the boiling point, where $\Delta G = 0$.

$T = \Delta H^0/\Delta S^0 = 63.11/.148 = 426$ K = 153 C

**6.16)**

$Ksp = x(4x)4(1\cdot10^{-6})^6 = 2.3\cdot10^{-69}$

$x = \{(2.3\cdot10^{-69})/(4)^4(1\cdot10^{-6})^6\}^{1/5} = 9.8\cdot10^{-8}$ M = $[SO_4^{2-}]$

$[Cu^{2+}] = 4x = 3.9\cdot10^{-7}$ M

**6.17)**

a)

Ksp = $[Zn^{2+}]^2[Fe(CN)_6^{4-}]$
Assuming $Zn_2Fe(CN)_6$ is the only source of $Zn^{2+}$ and $Fe(CN)_6^{4-}$ in solution, then
$[Zn^{2+}]$ = 0.10 mM

Ksp = $(1.0*10^{-4}\ M)^2\ [Fe(CN)_6^{4-}] = 2.1*10^{-16}$ =
$[Fe(CN)_6^{4-}] = 2.1*10^{-8}$ M

c)

What concentration of $K_4Fe(CN)_6$ must be added to a saturated solution of $Zn_2Fe(CN)_6$ to give a $[Zn^{+2}]$ of $5.0*10^{-7}$ M?

Ksp = $2.1*10^{-16} = [Zn^{2+}]^2[Fe(CN)_6^{4-}]$
Ksp = $2.1*10^{-16} = (5.0*10^{-7})^2[Fe(CN)_6^{4-}]$

$[Fe(CN)_6^{4-}] = (2.1*10^{-16}/(5.0*10^{-7})^2) = 8.4*10^{-4}$ M $Fe(CN)_6^{4-}$

$8.4*10^{-4}$ mol $K_4Fe(CN)_6$ /L would provide a $[Fe(CN)_6^{4-}]$ of $8.4*10^{-4}$ M.

**6.19)**

| | |
|---|---|
| Ksp(CaSO4) | 2.40E-05 |
| Ksp(Ag2SO4) | 1.50E-05 |

a)

At 99% precipitated, $[Ca^{2+}]$ = 0.0005 M and
so $[SO_4^{2-}]$ = 0.0480 M
$Ksp(Ag_2SO_4) < 4.32\cdot10^{-5} = (0.030)^2(.0480)$
Therefore, $Ag_2SO_4$ will precipitate before 99 % of the $Ca^{2+}$ reacts.

b)
$[SO_4^{2-}]$ when $AgSO_4$ starts to precipitate $= Ksp(Ag_2SO_4) / (0.03)^2$
$= 1.67 \cdot 10^{-2}$ M

$[Ca^{2+}] = Ksp(CaSO_4)/[SO_4^{2-}] = 1.44 \cdot 10^{-3}$ M

**6.25)**

$[Zn^{2+}] = 3.0 \cdot 10^{-16}/(3.2 \cdot 10^{-7})^2 = 2.93 \cdot 10^{-3}$ M

$\beta_1 = [Zn(OH)^+] / [Zn^{2+}][OH^-]$
$[Zn(OH)^+] \quad = \beta_1[Zn^{2+}][OH^-] = (2.5 \cdot 10^4)(2.93 \cdot 10^{-3})(3.2 \cdot 10^{-7})$
$= 2.3 \cdot 10^{-5}$ M

$\beta_3 = [Zn(OH)_3^-] / [Zn^{2+}][OH^-]^3$
$[Zn(OH)_3^-] \quad = \beta_3[Zn^{2+}][OH^-]^3 = (7.2 \cdot 10^{15})(2.93 \cdot 10^{-3})(3.2 \cdot 10^{-7})^3$
$= 6.9 \cdot 10^{-7}$ M

$\beta_4 = [Zn(OH)_4^{2-}] / [Zn^{2+}][OH^-]^4$
$[Zn(OH)_4^{2-}] \quad = \beta_3[Zn^{2+}][OH^-]^4 = (2.8 \cdot 10^{15})(2.93 \cdot 10^{-3})(3.2 \cdot 10^{-7})^4$
$= 8.6 \cdot 10^{-14}$ M

**6.30 (6:31 in 7th Ed)**
The following equilibria act to lower the pH.

$CO_2(g) \leftrightarrow CO_2(aq)$
$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq)$
$H_2CO_3(aq) + H_2O \leftrightarrow HCO_3^-(aq) + H_3O^+$

**6.35)**

| | a) | b) |
|---|---|---|
| acid | $H_3N^+CH_2CH_2N^+H_3$ | benzoic acid |
| conjugate base | $H_3N^+CH_2CH_2NH_2$ | benzoate |
| base | $H_2O$ | pyridine |
| conjugate acid | $H_3O^+$ | pyridinium |

**6.36)**

a) pH = -log(0.0100) = 2.000
b) pH = $-\log(1.01\cdot10^{-14}/0.035) = 12.54$
c) pH = -log(0.030) = 1.52
d) pH = -log(3.0) = -0.48
e) pH = $-\log(1.01\cdot10^{-14}/0.010) = 12.00$

**6.48)**

$CN^- + H_2O \leftrightarrow HCN + OH^-$
$K_b = Kw/Ka = (1.01\cdot10^{-14}/6.2\cdot10^{-10}) = 1.6\cdot10^{-5}$ M

**6.49)**

$K_{a2}$ $H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$

$K_{b2}$ $HC_2O_4^- + H_2O \leftrightarrow H_2C_2O_4 + OH^-$

**6-53)**

Write all the known quantities

$pCO_2$ = 01.0 atm
$[H^+] = 1.8*10^{-7}$ M
Volume = 2.00 L
You have a saturated solution of aragonite

You need to obtain $[Ca^{+2}]$ and than convert it to grams Ca in 2.00 L of water. To calculate $[Ca^{+2}]$ we need to have an equation that contains only $Ca^{+2}$ and other known quantities. Arrange the given equations in such a way that the unknown quantities will subtract out.

| | |
|---|---|
| $CaCO_3(s) \leftrightarrow Ca^{+2}(aq) + CO_3^{2-}(aq)$ | $Ksp = 6.0*10^{-9}$ |
| $CO_3^{-2}(aq) + H^+(aq) \leftrightarrow HCO_3^-(aq)$ | $1/K_2 = 1/4.7*10^{-11}$ |
| $CO_2(aq) + H_2O \leftrightarrow HCO_3^-(aq) + H^+(aq)$ | $1/K_1 = 1/4.4*10^{-7}$ |
| $CO_2(aq) \leftrightarrow CO_2(g)$ | $1/K_{CO2} = 1/\ 3.4*10^{-2}$ |

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$CaCO_3(s) + 2H^+(aq) \leftrightarrow CO_2(g) + Ca^{+2}(aq)$

$$K = Ksp/(K_1K_2K_{CO2}) = 8.5*10^9 = pCO_2[Ca^{+2}]/[H+]^2$$

$$= 8.5*10^9 = (0.10)[Ca^{+2}]/(1.8*10^{-7})^2$$

$[Ca^{+2}]$ on planet Aragonose = $2.8*10^{-3}$ M

$(2.00\ L/1)*(2.8*10^{-3}\ mol/L)*(40.078\ g\ Ca/mol) = 0.22$ g Ca in 2.00 L of seawater

## 6-56)

I used successive approximation in Excel.

| | | |
|---|---|---|
| [K]i | 3.00E+48 | |
| [IO3-]i | 1.00E-03 | M |
| [I-]i | 1.00E-03 | M |
| [H+]i | 1.00E-03 | M |
| X | 1.67E-04 | M |
| [IO3-]I - x | 8.33E-04 | M |
| [I-]I - 5x | 1.67E-04 | M |
| [H+] - 6x | 8.50E-07 | M |
| [I2] = 3x | 5.00E-04 | M |

Problems from the 6th ed

## 6-16)

Calculate the concentrations of Ag+ in each of the three saturated solutions.

$AgCl \leftrightarrow Ag^+ + Cl^-$

$Ksp = 1.8*10^{-10} = [Ag^+][Cl^-]$

Assuming the AgCl is the only source of $Ag^+$ and $Cl^-$ in the water, than $[Ag^+] = [Cl^-]$ (0.2 pts)

$Ksp = 1.8*10^{-10} = [Ag^+]^2$

$[Ag^+]_{AgCl} = 1.3*10^{-5}$ M

If you repeat this calculation for AgBr and AgI, you get

$[Ag^+]_{AgBr} = 7.1*10^{-7}$ M (0.2 pts)

$[Ag^+]_{AgI} = 9.1*10^{-9}$ M (0.2 pts)

Now you must convert each of these answers from units of mol/L to units of ng/ml

AgCl

$(1.3*10^{-5}$ mol/L)*(107.868 g Ag+/mol Ag)

$*(10^9 ng/g)*(1L/10^3 ml)$

= 1400 ng/ml or ppb (0.2 pts)

Repeat calculation for AgBr and AgI

AgBr gives 77 ppb and AgI gives 0.98 ppb (0.4 pts)

So, a saturated solution of AgBr will give a [Ag+] in the needed range. (0.4 pts)

**6-19)**

a)

The solubility of $CaSO_4$ is defined as the grams of $CaSO_4$ that dissolves in 1.0 L of water. From App F the $Ksp(CaSO_4) = 2.4*10^{-5}$.
$Ksp = 2.4*10^{-5} = [Ca^{2+}][SO_4^{2-}]$ (0.25 pts)

Assuming $CaSO_4$ is the only source of $Ca^{2+}$ and $SO_4^{2-}$ in solution, then $[Ca^{2+}] = [SO_4^{2-}]$ (0.25 pts)

$Ksp = 2.4*10^{-5} = [Ca^{2+}][SO_4^{2-}] = [SO_4^{2-}]^2$
$[SO_4^{2-}] = 4.9 *10^{-3}$ M (0.25 pts)

One mole of $SO_4^{2-}$ is formed for every one mole of $CaSO_4$ that dissolves, so the solubility of $CaSO_4$ is
($4.9*10^{-3}$ mol $CaSO_4$ dissolves/L)*(136.14 g $CaSO_4$/1 mol) = 0.67 g $CaSO_4$/L (0.25 pts)

b)

| | $[Ca^{+2}]$ | $[SO_4^{2-}]$ |
|---|---|---|
| Initial | 0.50 | 0 |
| @ equilibrium | 0.50 + x | x (0.2 pts) |

Ksp = $2.4*10^{-5} = [Ca^{2+}][SO_4^{2-}] = (0.5+x)x$ (0.2 pts)
Assume $0.5 + x \approx 0.5$ (0.1 pts)
$2.4*10^{-5} = 0.5x$
$x = [SO_4^{2-}] = 4.8*10^{-5}$ M (0.2 pts)
assumption valid: $0.5 + 4.8*10^{-5} \approx 0.5$ (0.1 pts)

($4.8*10^{-5}$ mol $CaSO_4$ dissolves/L)*(136.14 g $CaSO_4$/1 mol) = 0.0065 g $CaSO_4$/L or 6.5 mg/L (0.2 pts)