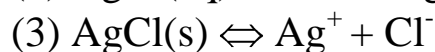
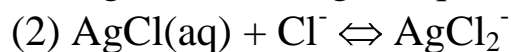
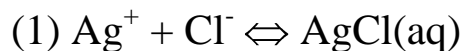


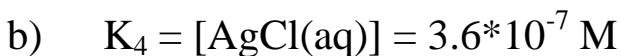
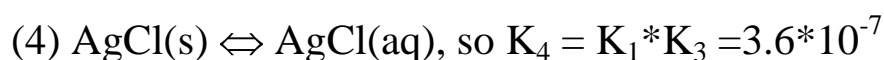
Homework set #1**CHEM 311**

6-A



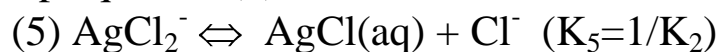
a)

add equations 1 and 3 to get



c)

flip equation (2)



flip equation (4)



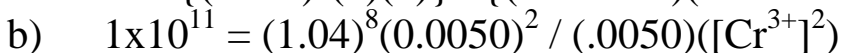
add equations (5) and (6) to get



so $K_7 = K_5 K_6 = 1/(K_2 K_4) = 1/(K_1 K_2 K_3) = 3.0 * 10^4 \text{ M}$

6B

$$K = \{(1+8x)^8 (x)(x)\} / \{(0.0100-x)(0.0100-2x)^2\}$$



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

6D

- a) $\text{Ca}(\text{IO}_3)_2$
 $K_{sp} = [\text{Ca}^{+2}][\text{IO}_3^-]^2$
If the $\text{Ca}(\text{IO}_3)_2$ is the only source of Ca^{+2} and IO_3^- in solution,
than $[\text{IO}_3^-] = 2[\text{Ca}^{+2}]$
 $K_{sp} = [\text{Ca}^{+2}](2[\text{Ca}^{+2}])^2 = 4[\text{Ca}^{+2}]^3 = 7.1 \times 10^{-7}$
 $[\text{Ca}^{+2}] = 5.6 \times 10^{-3} \text{ M}$
 $5.6 \times 10^{-3} \text{ mol Ca}(\text{IO}_3)_2 \text{ dissolve per Liter}$

- $\text{Ba}(\text{IO}_3)_2$
 $K_{sp} = [\text{Ba}^{+2}][\text{IO}_3^-]^2$
If the $\text{Ba}(\text{IO}_3)_2$ is the only source of Ba^{+2} and IO_3^- in solution,
than $[\text{IO}_3^-] = 2[\text{Ba}^{+2}]$
 $K_{sp} = [\text{Ba}^{+2}](2[\text{Ba}^{+2}])^2 = 4[\text{Ba}^{+2}]^3 = 1.5 \times 10^{-9}$
 $[\text{Ba}^{+2}] = 7.2 \times 10^{-4} \text{ M}$
 $7.2 \times 10^{-4} \text{ mol Ba}(\text{IO}_3)_2 \text{ dissolve per Liter}$

$\text{Ca}(\text{IO}_3)_2$ is more soluble

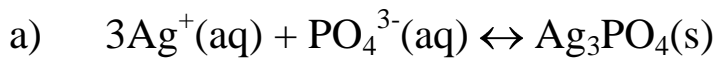
- b) $\text{Ca}(\text{NO}_3)_2$

6H

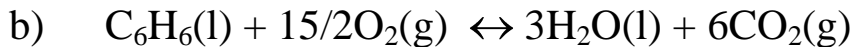
- a) neutral
b) CH_3CO_2^- is the conjugate base of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, (basic)
c) NH_4^+ is the conjugate acid of ammonia NH_3 , (acidic)
d) PO_4^{3-} is a weak base, (basic)
e) neutral, $(\text{CH}_3)_4\text{N}^+$ can not accept or donate a proton in water
f) $\text{C}_6\text{H}_5\text{CO}_2^-$ 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 so 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 $^{87}\text{Rb} / ^{87}\text{Sr}$ measured today will be about the same as the ratio measured a year from now, but the reaction is thermodynamically favorable.

6-4



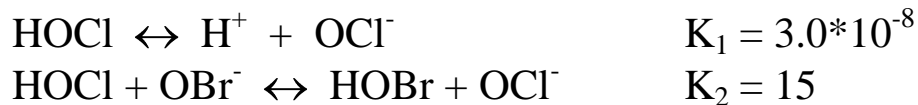
$$K = 1 / ([\text{Ag}^+]^3[\text{PO}_4^{3-}])$$



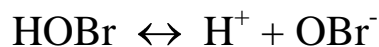
$$K = P_{\text{CO}_2}^6 / P_{\text{O}_2}^{15/2}$$

C_6H_6 and water do not go into the equilibrium expression because they are not in a dilute solution. They are in their pure forms, and so their concentrations are their densities, which are constants. 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.

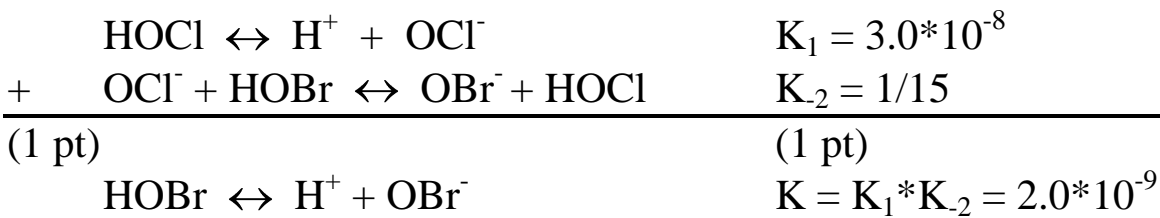
6.6



What is the K for the following reaction?



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



6-9

- a) right
- b) neither
- c) right
- d) larger

6-10

a) $K = p_{\text{H}_2\text{O}}$

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

$$\Delta G^0 = 63.11 - 298 \cdot (.148) = 19.10 \text{ kJ/mol}$$

$$K_p = e^{-\Delta G^0/RT} = e^{-(19100/(8.314 \cdot 298))} = 0.000391 \text{ bar}$$

b)

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

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

6.16)

$$K_{sp} = x(4x)^4(1 \cdot 10^{-6})^6 = 2.3 \cdot 10^{-69}$$

$$x = \{(2.3 \cdot 10^{-69})/(4)^4(1 \cdot 10^{-6})^6\}^{1/5} = 9.8 \cdot 10^{-8} \text{ M} = [\text{SO}_4^{2-}]$$

$$[\text{Cu}^{2+}] = 4x = 3.9 \cdot 10^{-7} \text{ M}$$

6.17)

a)

$$K_{sp} = [\text{Zn}^{2+}]^2 [\text{Fe}(\text{CN})_6^{4-}]$$

Assuming $\text{Zn}_2\text{Fe}(\text{CN})_6$ is the only source of Zn^{2+} and $\text{Fe}(\text{CN})_6^{4-}$ in solution, then

$$[\text{Zn}^{2+}] = 0.10 \text{ mM}$$

$$K_{sp} = (1.0 \times 10^{-4} \text{ M})^2 [\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-16} \quad =$$

$$[\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-8} \text{ M}$$

c)

What concentration of $\text{K}_4\text{Fe}(\text{CN})_6$ must be added to a saturated solution of $\text{Zn}_2\text{Fe}(\text{CN})_6$ to give a $[\text{Zn}^{2+}]$ of $5.0 \times 10^{-7} \text{ M}$?

$$K_{sp} = 2.1 \times 10^{-16} = [\text{Zn}^{2+}]^2 [\text{Fe}(\text{CN})_6^{4-}]$$

$$K_{sp} = 2.1 \times 10^{-16} = (5.0 \times 10^{-7})^2 [\text{Fe}(\text{CN})_6^{4-}]$$

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

$8.4 \times 10^{-4} \text{ mol K}_4\text{Fe}(\text{CN})_6/\text{L}$ would provide a $[\text{Fe}(\text{CN})_6^{4-}]$ of $8.4 \times 10^{-4} \text{ M}$.

6.19)

$$K_{sp}(\text{CaSO}_4) \quad 2.40\text{E-}05$$

$$K_{sp}(\text{Ag}_2\text{SO}_4) \quad 1.50\text{E-}05$$

a)

At 99% precipitated, $[\text{Ca}^{2+}] = 0.0005 \text{ M}$ and

so $[\text{SO}_4^{2-}] = 0.0480 \text{ M}$

$$K_{sp}(\text{Ag}_2\text{SO}_4) < 4.32 \cdot 10^{-5} = (0.030)^2 (0.0480)$$

Therefore, Ag_2SO_4 will precipitate before 99 % of the Ca^{2+} reacts.

b)

$$[\text{SO}_4^{2-}] \text{ when AgSO}_4 \text{ starts to precipitate} = K_{\text{sp}}(\text{Ag}_2\text{SO}_4) / (0.03)^2 \\ = 1.67 \cdot 10^{-2} \text{ M}$$

$$[\text{Ca}^{2+}] = K_{\text{sp}}(\text{CaSO}_4) / [\text{SO}_4^{2-}] = 1.44 \cdot 10^{-3} \text{ M}$$

6.25)

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

$$\beta_1 = [\text{Zn}(\text{OH})^+] / [\text{Zn}^{2+}][\text{OH}^-]$$

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

$$\beta_3 = [\text{Zn}(\text{OH})_3^-] / [\text{Zn}^{2+}][\text{OH}^-]^3$$

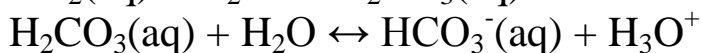
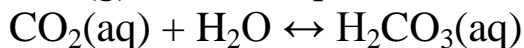
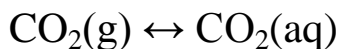
$$[\text{Zn}(\text{OH})_3^-] = \beta_3 [\text{Zn}^{2+}][\text{OH}^-]^3 = (7.2 \cdot 10^{15})(2.93 \cdot 10^{-3})(3.2 \cdot 10^{-7})^3 \\ = 6.9 \cdot 10^{-7} \text{ M}$$

$$\beta_4 = [\text{Zn}(\text{OH})_4^{2-}] / [\text{Zn}^{2+}][\text{OH}^-]^4$$

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

6.30 (6:31 in 7th Ed)

The following equilibria act to lower the pH.



6.35)

	a)	b)
acid	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$	benzoic acid
conjugate base	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2$	benzoate
base	H_2O	pyridine
conjugate acid	H_3O^+	pyridinium

6.36)

a) $\text{pH} = -\log(0.0100) = 2.000$

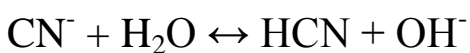
b) $\text{pH} = -\log(1.01 \cdot 10^{-14} / 0.035) = 12.54$

c) $\text{pH} = -\log(0.030) = 1.52$

d) $\text{pH} = -\log(3.0) = -0.48$

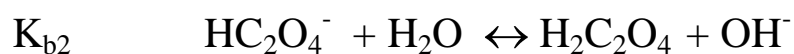
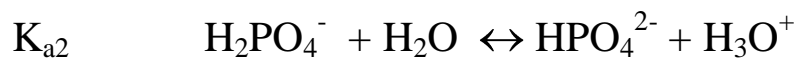
e) $\text{pH} = -\log(1.01 \cdot 10^{-14} / 0.010) = 12.00$

6.48)



$$K_b = K_w / K_a = (1.01 \cdot 10^{-14} / 6.2 \cdot 10^{-10}) = 1.6 \cdot 10^{-5} \text{ M}$$

6.49)



6-53)

Write all the known quantities

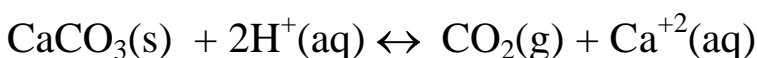
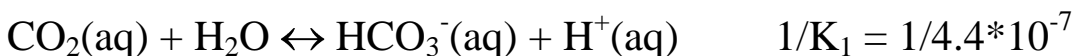
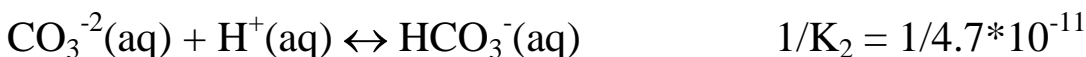
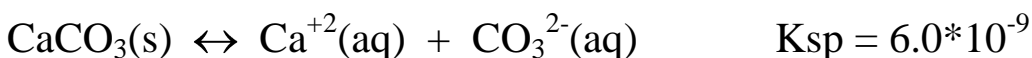
$$p\text{CO}_2 = 01.0 \text{ atm}$$

$$[\text{H}^+] = 1.8 \cdot 10^{-7} \text{ M}$$

$$\text{Volume} = 2.00 \text{ L}$$

You have a saturated solution of aragonite

You need to obtain $[\text{Ca}^{+2}]$ and then convert it to grams Ca in 2.00 L of water. To calculate $[\text{Ca}^{+2}]$ 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.



$$K = K_{\text{sp}}/(K_1 K_2 K_{\text{CO}_2}) = 8.5 \cdot 10^9 = p\text{CO}_2 [\text{Ca}^{+2}]/[\text{H}^+]^2$$

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

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

$$(2.00 \text{ L}/1) \cdot (2.8 \cdot 10^{-3} \text{ mol/L}) \cdot (40.078 \text{ g Ca/mol}) = 0.22 \text{ g Ca}$$

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+]i - 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.



$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

Assuming the AgCl is the only source of Ag⁺ and Cl⁻ in the water, then $[\text{Ag}^+] = [\text{Cl}^-]$ (0.2 pts)

$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^+]^2$$

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

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

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

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

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

AgCl

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

$$*(10^9 \text{ ng/g})*(1\text{L}/10^3 \text{ ml})$$

$$= 1400 \text{ ng/ml or ppb (0.2 pts)}$$

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 CaSO₄ is defined as the grams of CaSO₄ that dissolves in 1.0 L of water. From App F the

$$K_{sp}(\text{CaSO}_4) = 2.4 * 10^{-5}.$$

$$K_{sp} = 2.4 * 10^{-5} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \text{ (0.25 pts)}$$

Assuming CaSO₄ is the only source of Ca²⁺ and SO₄²⁻ in solution, then $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$ (0.25 pts)

$$K_{sp} = 2.4 * 10^{-5} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = [\text{SO}_4^{2-}]^2$$

$$[\text{SO}_4^{2-}] = 4.9 * 10^{-3} \text{ M (0.25 pts)}$$

One mole of SO₄²⁻ is formed for every one mole of CaSO₄ that dissolves, so the solubility of CaSO₄ is
 $(4.9 * 10^{-3} \text{ mol CaSO}_4 \text{ dissolves/L}) * (136.14 \text{ g CaSO}_4 / 1 \text{ mol}) = 0.67 \text{ g CaSO}_4 / \text{L}$ (0.25 pts)

b)

	[Ca ⁺²]	[SO ₄ ²⁻]
Initial	0.50	0
@ equilibrium	0.50 + x	x (0.2 pts)

$$K_{sp} = 2.4 \times 10^{-5} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (0.5+x)x \quad (0.2 \text{ pts})$$

$$\text{Assume } 0.5 + x \approx 0.5 \quad (0.1 \text{ pts})$$

$$2.4 \times 10^{-5} = 0.5x$$

$$x = [\text{SO}_4^{2-}] = 4.8 \times 10^{-5} \text{ M} \quad (0.2 \text{ pts})$$

$$\text{assumption valid: } 0.5 + 4.8 \times 10^{-5} \approx 0.5 \quad (0.1 \text{ pts})$$

$$(4.8 \times 10^{-5} \text{ mol CaSO}_4 \text{ dissolves/L}) * (136.14 \text{ g CaSO}_4 / 1 \text{ mol}) = \\ 0.0065 \text{ g CaSO}_4 / \text{L} \text{ or } 6.5 \text{ mg/L} \quad (0.2 \text{ pts})$$