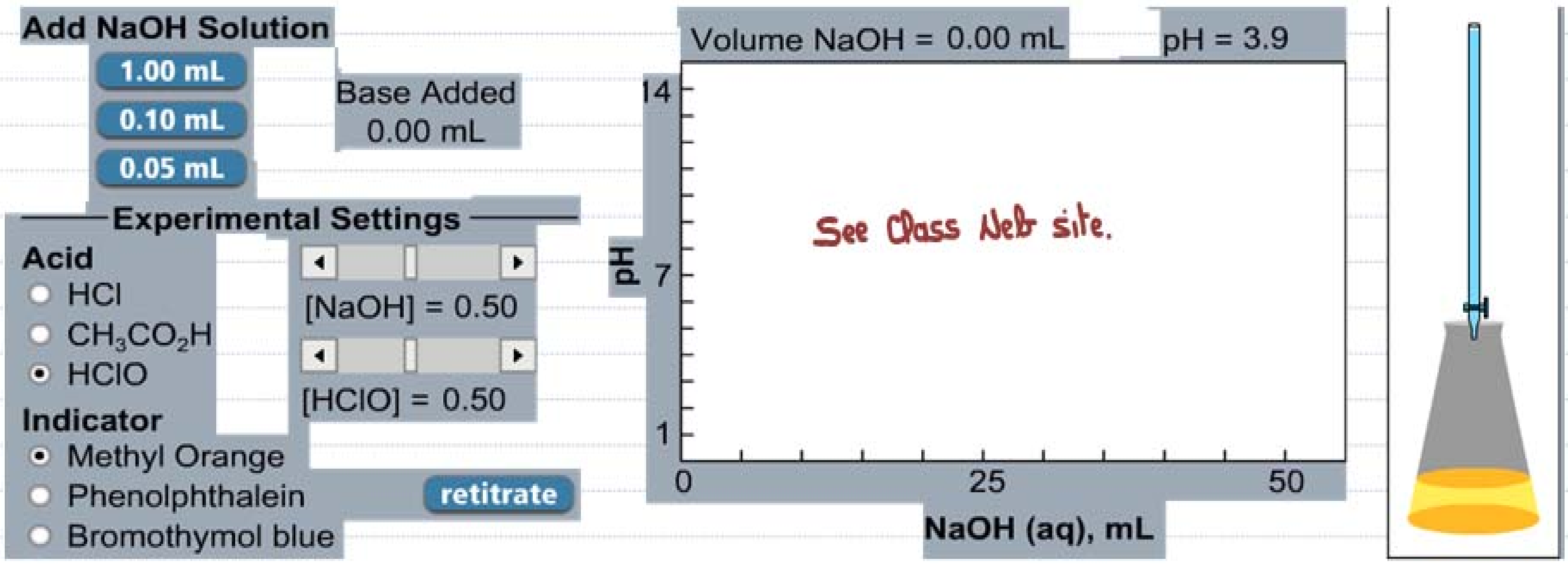
Announcements – Lecture XIX – Tuesday, Apr 10th

1. iClicker:  Pick any letter a-e

17.3 Acid-Base Titrations

Weak Acid/Strong Base

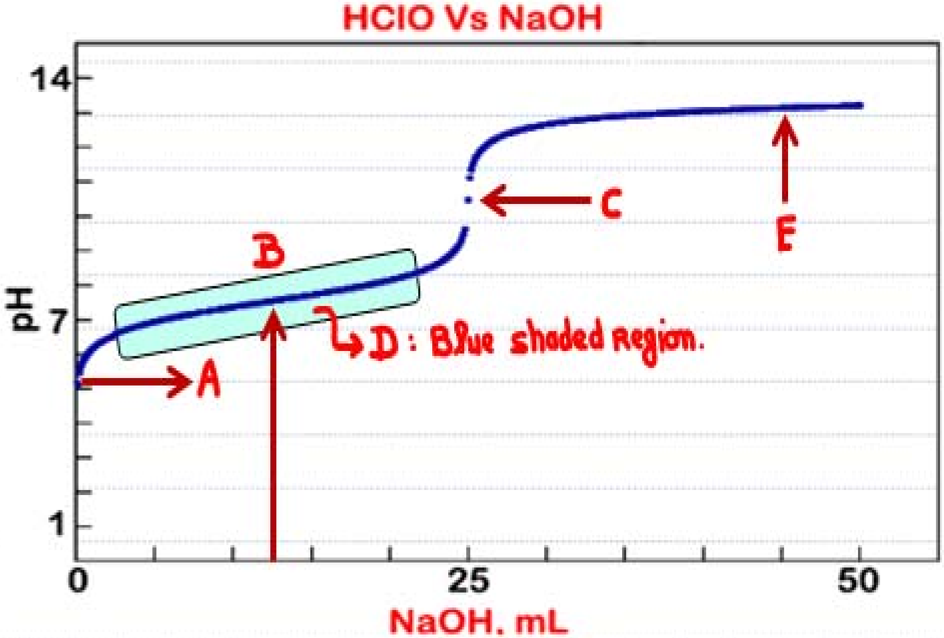
Choose: 0.5M HClO vs 0.5M NaOH



17.3 Acid-Base Titrations

Weak Acid/Strong Base

$HClO(aq) + NaOH(aq) = NaClO(aq) + H_2O(l)$: K_a HClO = 3.5×10^{-8}



A : $HClO(aq) + H_2O(l) \Leftrightarrow H_3O^+ + ClO^-$

B : [Buffer base] = [Buffer acid]

$[ClO^-]$ = $[HClO]$

pH = pKa of HClO

D : Buffer Region : $pH = pK_a + \log_{10} \frac{[\text{Buffer base}]}{[\text{Buffer acid}]}$

E : $NaOH(aq) = Na^+ + OH^-$

$pOH = -\log_{10}[OH^-]$

$pH = 14 - pOH$

C : Equivalence point, pH depends on hydrolysis

$NaClO(aq) = Na^+ + ClO^-$

Na^+ ↓ Neutral cation. ClO^- ↓ Basic anion.

$ClO^- + H_2O(l) \Leftrightarrow HClO(aq) + OH^-$

$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{3.5 \times 10^{-8}}$

Calculate pOH

$pH = 14 - pOH$

18.1 Solubility Equilibria and Ksp

The Solubility Product Constant

Compound	K_{sp} at 25 °C
$PbBr_2$	6.3×10^{-6}
AgBr	3.3×10^{-13}
$CaCO_3$	3.8×10^{-9}
$CuCO_3$	2.5×10^{-10}
$NiCO_3$	6.6×10^{-9}
Ag_2CO_3	8.1×10^{-12}
$PbCl_2$	1.7×10^{-5}
AgCl	1.8×10^{-10}
BaF_2	1.7×10^{-6}
CaF_2	3.9×10^{-11}
$Cu(OH)_2$	1.6×10^{-19}
$Fe(OH)_3$	6.3×10^{-38}
$Ni(OH)_2$	2.8×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Ca_3(PO_4)_2$	1.0×10^{-25}
$CaSO_4$	2.4×10^{-5}
$PbSO_4$	1.8×10^{-8}

$$PbBr_2(s) \rightleftharpoons Pb^{2+} + 2Br^-$$

Remember that pure liquids and solids do not appear in an equilibrium expression.

$$K = [Pb^{2+}][Br^-]^2$$

↑

K_{sp} : Solubility Product Constant.

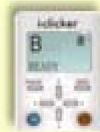
Note that the salts listed are those during Chem 111 using Solubility Guide Lines we would have considered insoluble.

Looking at the Ksp values, these are all reactant-favored equilibria

18.2 Using Ksp in Calculations

Estimating Solubility

Which of the following salts is the **least soluble** in water?



a) AgBr — $K_{sp} = 3.3 \times 10^{-13}$ @25°C

b) $Cu(OH)_2$ ✓ — $K_{sp} = 1.6 \times 10^{-19}$ @25°C

c) $Ca_3(PO_4)_2$ — $K_{sp} = 1.0 \times 10^{-25}$ @25°C

	AgBr(s)	⇔	Ag^+	+	Br^-
I	Some		0		0
C	−s		s		s
E			s		s

$K_{sp} = [Ag^+][Br^-]$:

$3.3 \times 10^{-13} = (s)(s)$

$s^2 = 3.3 \times 10^{-13}$

$s = \sqrt{3.3 \times 10^{-13}} = 5.47 \times 10^{-7}$

	$Cu(OH)_2$(s)	⇔	Cu^{2+}	+	$2\ OH^-$
I	Some		0		0
C	−s		s		2s
E			s		2s

$K_{sp} = [Cu^{2+}][OH^-]^2$

$1.6 \times 10^{-19} = (s)(2s)^2$

$4s^3 = 1.6 \times 10^{-19}$

$s^3 = 4.0 \times 10^{-20}$

$s = \sqrt[3]{4.0 \times 10^{-20}} = 3.42 \times 10^{-7}$

	$Ca_3(PO_4)_2$(s)	⇔	$3\ Ca^{2+}$	+	$2\ PO_4^{3-}$
I	Some		0		0
C	−s		3s		2s
E			3s		2s

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$1.0 \times 10^{-25} = (3s)^3(2s)^2$

$108 s^5 = 1.0 \times 10^{-25}$

$s^5 = 9.3 \times 10^{-28}$

$s = \sqrt[5]{9.3 \times 10^{-28}} = 3.9 \times 10^{-6}$

18.2 Using Ksp in Calculations

Estimating Solubility

General Formula	Example	K_{sp} Expression	K_{sp} as a Function of Molar Solubility (x)	Solubility (x) as a Function of K_{sp}
MY	AgCl	$K_{sp} = [M^+][Y^-]$	$K_{sp} = (x)(x) = x^2$	$x = \sqrt{K_{sp}}$
MY_2	HgI_2	$K_{sp} = [M^{2+}][Y^-]^2$	$K_{sp} = (x)(2x)^2 = 4x^3$	$x = \sqrt[3]{\frac{K_{sp}}{4}}$
MY_3	BiI_3	$K_{sp} = [M^{3+}][Y^-]^3$	$K_{sp} = (x)(3x)^3 = 27x^4$	$x = \sqrt[4]{\frac{K_{sp}}{27}}$
M_2Y_3	$Fe_2(SO_4)_3$	$K_{sp} = [M^{3+}]^2[Y^{2-}]^3$	$K_{sp} = (2x)^2(3x)^3 = 108x^5$	$x = \sqrt[5]{\frac{K_{sp}}{108}}$

Instead of memorizing these simply use the ICE method.

Note that in the ICE table for solubility we use 's' instead of 'x' simply because by solving for s, we have determined the solubility in mol.L⁻¹ ... M

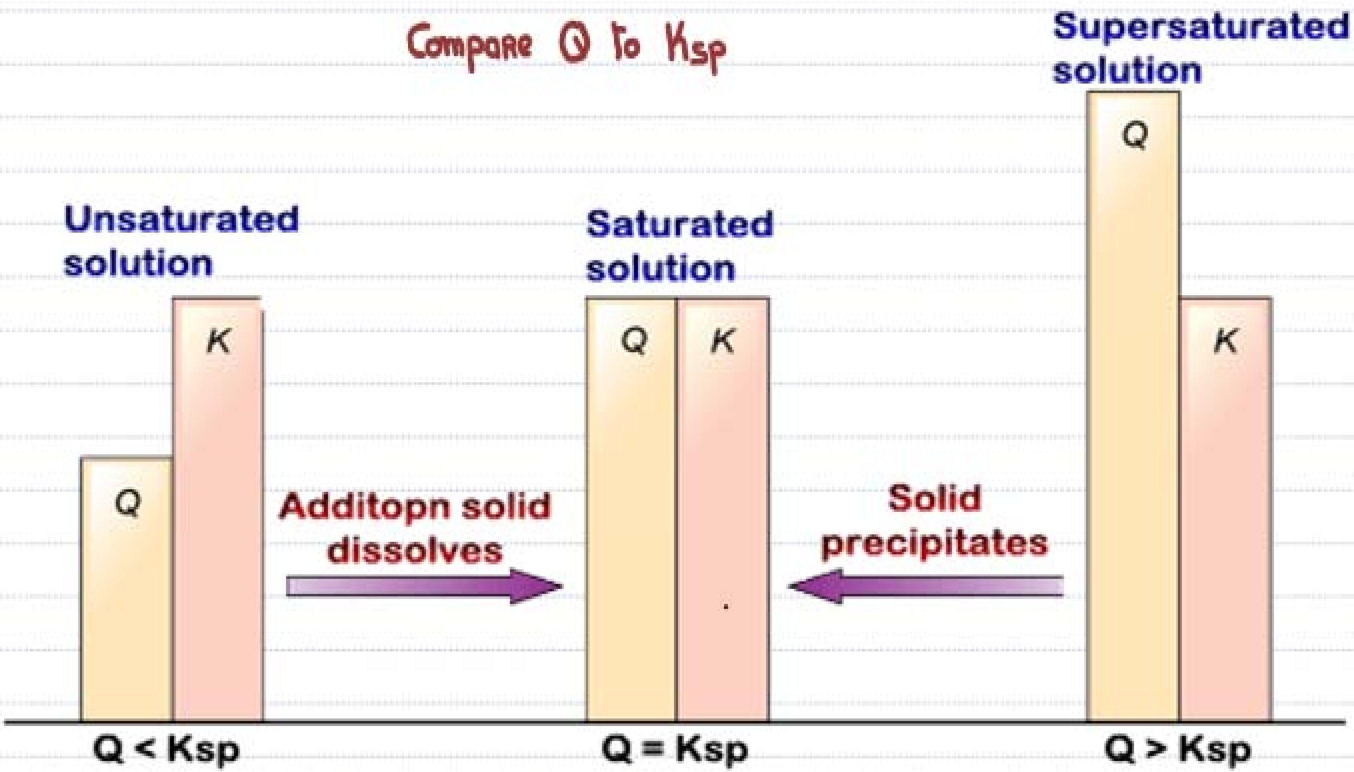
18.2 Using Ksp in Calculations

Predicting Whether a Solid Will Precipitate or Dissolve

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

$$Q = [Ag^+][Cl^-]$$

Compare Q to Ksp



18.2 Using Ksp in Calculations

Predicting Whether a Solid Will Precipitate or Dissolve

When 25.0 mL of a 7.02×10^{-4} M iron(III) bromide solution is combined with 22.0 mL of a 2.10×10^{-4} M sodium sulfide solution does a precipitate form?

Ksp Iron(III) sulfide = 1.4×10^{-88}

a) Yes ✓

b) No

$Fe_2S_3(s) \rightleftharpoons 2\,Fe^{3+} + 3\,S^{2-}$

$Q = [Fe^{3+}]^2[S^{2-}]^3$

Total volume when solutions are mixed 25 + 22 = 47 mL

$[Fe^{3+}]$:

$\#\text{mol } FeBr_3 = 7.02 \times 10^{-4}(0.025)$
$= 1.755 \times 10^{-5}$

$FeBr_3(aq) = Fe^{3+} + 3Br^-$

$\#\text{mol } Fe^{3+} = 1.755 \times 10^{-5}$
$[Fe^{3+}] = 1.755 \times 10^{-5}/0.047 = 3.73 \times 10^{-4}$

$[S^{2-}]$

$\#\text{mol } Na_2S = 2.10 \times 10^{-4}(0.022)$
$= 4.62 \times 10^{-6}$

$Na_2S(aq) = 2\,Na^+ + S^{2-}$

$\#\text{mol } S^{2-} = 4.62 \times 10^{-6}$
$[S^{2-}] = 4.62 \times 10^{-6}/0.047 = 9.83 \times 10^{-5}$

$Q = (3.73 \times 10^{-4})^2(9.83 \times 10^{-5})^3$
$= 1.32 \times 10^{-19} > K_{sp}$

18.2 Using Ksp in Calculations

The Common Ion Effect

The Common Ion Effect

See Class Web Site.

Insoluble Salt

- ◉ $PbCl_2$
- ○ AgCl
- ○ CaF_2
- ○ $PbCrO_4$

0.01 g

Common Ion: Cl^-

Soluble Salt

- ◉ NaCl
- ○ KCl
- ○ $NaNO_3$
- ○ $Pb(NO_3)_2$

0.01 M

Solubility: 4.50 g/L

Precipitate: 0.00 g

$[Na^+]$ = 0.00 M

$[Cl^-]$ = 0.00 M

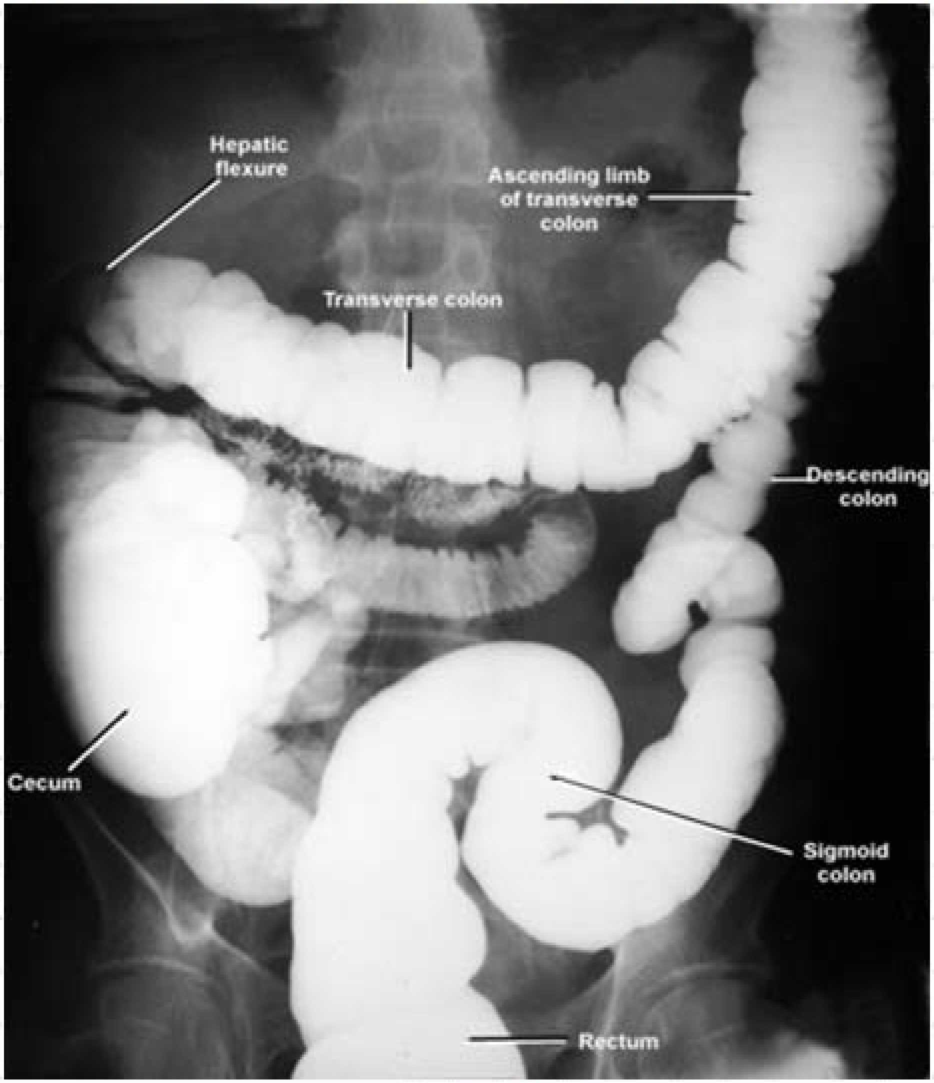
Equation: $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$

	Pb^{2+}	Cl^-
Initial Concentration (M)	0.00 M	0.00 M
Change on proceeding to equilibrium	+x	+2x
Equilibrium concentration (M)	x	2x

Solubility = x = 1.62×10^{-2} mol/L

18.2 Using Ksp in Calculations

The Common Ion Effect – Barium Gastrointestinal Images



$BaSO_4(s) \Leftrightarrow Ba^{2+} + SO_4^{2-}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ @ 25°C

Toxicology : 1-15 g injested.

18.2 Using Ksp in Calculations

The Common Ion Effect

a) What is the solubility of $BaSO_4(s)$ in pure water? Ksp = 1.1×10^{-10} @ 25°C

b) What is the solubility of $BaSO_4(s)$ in 0.1M Na_2SO_4?

$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$

Expected shift ←

	$BaSO_4(s)$	$\rightleftharpoons$	Ba^{2+}	+	SO_4^{2-}
I	Some		0		0
C	-s		s		s
E			s		s

$Ksp = [Ba^{2+}][SO_4^{2-}]$

$1.1\times10^{-10} = (s)(s)$

$s^2 = 1.1\times10^{-10}$

$s = \sqrt{1.1\times10^{-10}} = 1.05\times10^{-5}\ mol.L^{-1}$

$Na_2SO_4(aq) = 2Na^{+} + SO_4^{2-}$

	$BaSO_4(s)$	$\rightleftharpoons$	Ba^{2+}	+	SO_4^{2-}
I	Some		0		0.1
C	-s		s		s
E			s		0.1+s

$[SO_4^{2-}]_i > 100\ Ksp$: $0.1+s \approx 0.1$

$Ksp = [Ba^{2+}][SO_4^{2-}]$

$1.1\times10^{-10} = s(0.1)$

$s = 1.1\times10^{-9}\ mol.L^{-1}$

$BaSO_4$: 233.4 $g.mol^{-1}$

$s = 0.0025\ g.L^{-1}$

$s = 0.00000026\ g.L^{-1}$

18.4 Simultaneous Equilibria

Solubility and pH – Remember me – Le Chatelier's Principle

HCN is a weak acid –

$HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+ + CN^-$ Kc = 4.0×10^{-10} @ 25°C

Addition of OH^- to this equilibrium will cause the $[CN^-]$ to

a) Increase ✓ c) Remain unchanged
b) Decrease d) Impossible to determine

At first look it looks like c) as OH^- is neither a product or a reactant.

$HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+ + CN^-$

$+$

$OH^- = H_2O(l)$

Net result is the removal of a product.

Shift towards products. $[CN^-]\uparrow$

18.4 Simultaneous Equilibria

Solubility and pH

→ Expected equilibrium shift.

$NiCO_3(s) \Leftrightarrow CO_3^{2-} + Ni^{2+}$; $K_{sp} = 1.3 \times 10^{-7}$ @ 25°C in pure water

+

Add acid: $H_3O^+ = HCO_3^- + H_2O(l)$; Strong acid + Weak base ... 100%

$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$ $K_a = 5.5 \times 10^{-11}$

Reverse: $H_3O^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + H_2O$ $K = 1.8 \times 10^{10}$ $(1/K_a)$

$NiCO_3(s)$	$\Leftrightarrow Ni^{2+} + CO_3^{2-}$	$K_{sp} = 1.3 \times 10^{-7}$
$H_3O^+ + CO_3^{2-}$	$\Leftrightarrow HCO_3^- + H_2O(l)$	$K = 1.8 \times 10^{10}$
$NiCO_3(s) + H_3O^+$	$\Leftrightarrow Ni^{2+} + HCO_3^- + H_2O(l)$	$K = 2.3 \times 10^{3}$