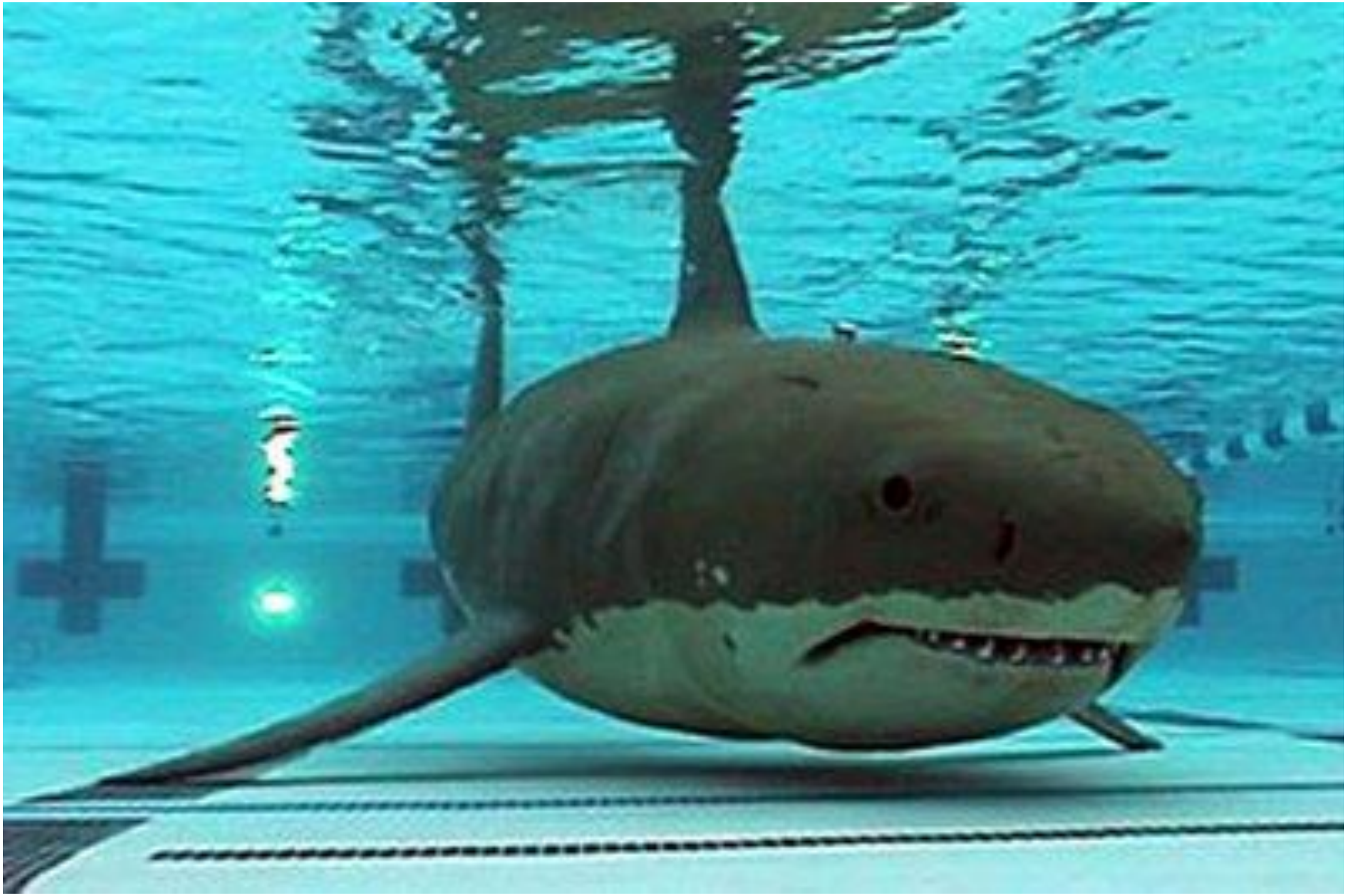
Buffers:



Buffers:

A buffer is an aqueous system that allows only small changes in pH on the addition of acids or bases.

Consider a system consisting of equal amounts of $HC_2H_3O_2$ and $C_2H_3O_2^-$.

If strong base added:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$$

If strong acid added:

$$C_2H_3O_2^-(aq) + H^+(aq) \rightarrow HC_2H_3O_2(aq)$$

Identifying Buffers:

Buffers consist of a weak acid and its corresponding conjugate base.

Ex: Is the system NH_3/NH_4Cl a buffer?

Ex: Is the system HCl/Cl^- a buffer?

Calculating the pH of Buffer Systems:

Ex:

Calculate the pH of a buffer consisting of 1 M NH_3 and 1 M NH_4Cl.

$K_B = 1.8 \times 10^{-5}$

Answer: pH = 9.26

Can use K_A or K_B to determine pH.

DIFFICULT!!!

Henderson-Hasselbach Equation:

$$pH = pK_A + \text{Log}\frac{[\text{base}]}{[\text{acid}]}$$

$$pH = pK_A + \text{Log}\frac{\text{moles of base}}{\text{moles of acid}}$$

Consider a buffer consisting of the weak acid HA and its conjugate base A^-.

$$pH = pK_A + \text{Log}\frac{[A^-]}{[HA]}$$

Where $pK_A = -\text{Log}(K_A)$

Buffer Examples cont…

Ex:2

What is the pH of a buffer prepared by dissolving 25.5 g of $NaC_2H_3O_2$ in 0.550 M $HC_2H_3O_2(aq)$ to prepare a 500.0 mL buffer? $K_A = 1.8\times10^{-5}$

Ex:3

What mass of $NaC_2H_3O_2$ must be dissolved in 300.0 mL of 0.250 M $HC_2H_3O_2$ to prepare a buffer of pH = 5.09?

Buffer Examples cont…

Ex:4

What is the effect of adding 0.025 moles of HCl to 500.0 mL of a buffer consisting of 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$? $K_A = 1.8\times10^{-5}$

HCl: STRONG ACID

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Buffer: $HC_2H_3O_2$ and $C_2H_3O_2^-$

NOTE: 0.500 L×0.100 M = 0.0500 mol

	From HCl		Buffer base		Buffer Acid
	H^+	$+$	$C_2H_3O_2^-$	$\rightarrow$	$HC_2H_3O_2$
I:	0.025 mol		0.0500 mol		0.0500 mol
C:	-0.025 mol		-0.025 mol		+0.025 mol
E:	0		0.0250 mol		0.0750 mol

NOTE: H^+ from HCl completely neutralized!!
Only buffer left.

Ex:5

What is the effect of adding 0.025 moles of NaOH to 500.0 mL of a buffer consisting of 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

$K_A = 1.8 \times 10^{-5}$

From

NaOH		Buffer Acid		Buffer Base
OH^-	+	$HC_2H_3O_2$	$\rightarrow$	$C_2H_3O_2^- + H_2O$
I: 0.025 mol		0.0500 mol		0.0500 mol
C: -0.025 mol		-0.025 mol		+0.025 mol
E: 0		0.0250 mol		0.0750 mol

Ex:6

What is the effect of adding 0.100 moles of HCl to 500.0 mL of a buffer consisting of 0.100 M $HC_2H_3O_2$ and 0.100 M NaC_2H_3O

From HCl		Buffer base		Buffer Acid
H^+	+	$C_2H_3O_2^-$	$\rightarrow$	$HC_2H_3O_2$
I: 0.100 mol		0.0500 mol		0.0500 mol
C: -0.0500 mol		-0.0500 mol		+0.0500 mol
E: 0.0500 mol		0		0.100 mol

NOTE: Buffer capacity exceeded!!

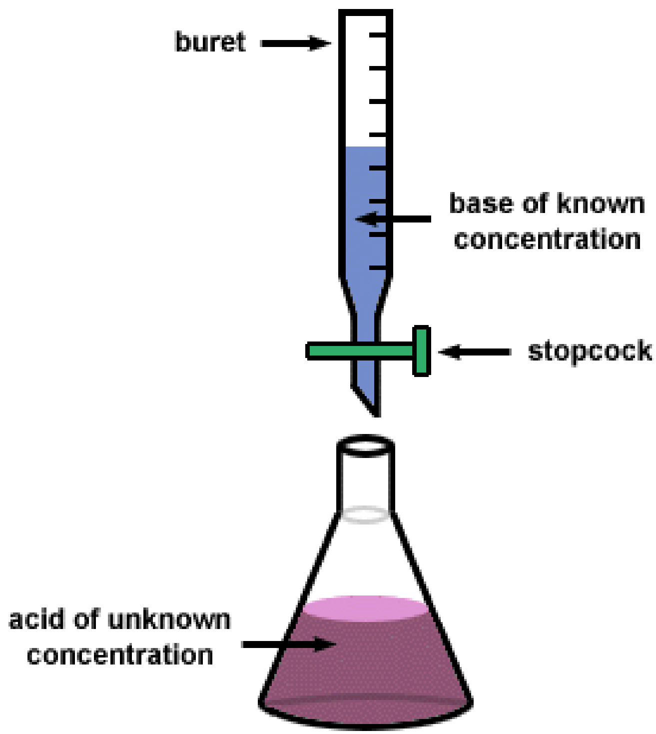
Acid-Base Titrations:

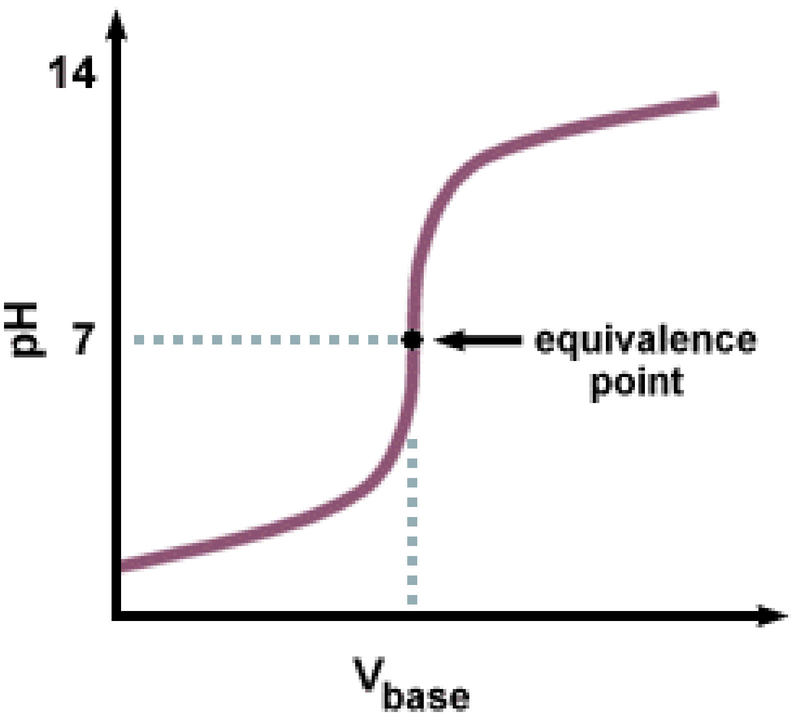
Types:

Strong Acid/Strong Base

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

? M KNOWN M



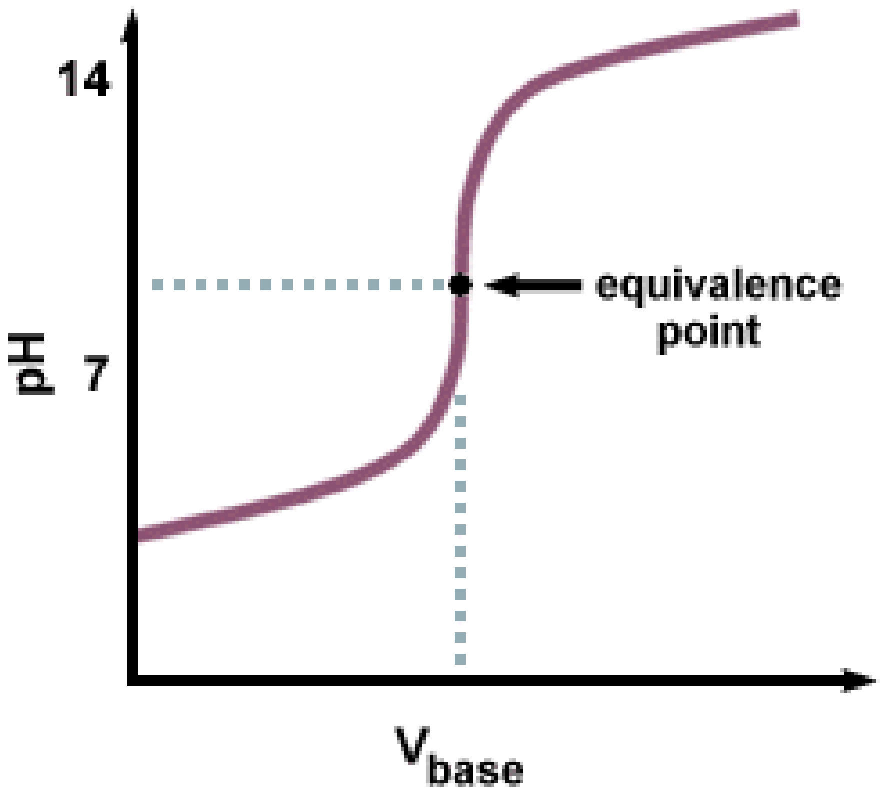


Acid-Base Titrations cont…:

Weak Acid/Strong Base

$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O$

? M KNOWN M



Predicting the pH of an Acid-Base Mixture:

Strong Base – Strong Acid

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

Ex:

Consider the titration of 25.0 mL of 1.00 M HCl with 1.00 M NaOH. Calculate the pH on the addition of 10.0 mL, 25.0 mL, and 40.0 mL of the NaOH solution.

Ex: Strong Base – Strong Acid:

10.0 mL of 1.00 M NaOH:

$$HCl \quad + \quad NaOH \quad \rightarrow \quad NaCl \quad + \quad H_2O$$

I	0.0250 mol	0.0100 mol	0	-
C	-0.0100 mol	-0.0100 mol	+0.0100 mol	+0.0100 mol
F	0.0150 mol	0	0.0100 mol	0.0100 mol

[HCl] = 0.0150 mol/0.0350 L = 0.429 M

Thus pH = 0.368

Ex: Strong Base – Strong Acid:

25.0 mL of 1.00 M NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

I	0.0250 mol	0.0250 mol	0	-
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	+0.0250 mol
F	0	0	0.0250 mol	0.0250 mol

Equivalence point. Only salt water present.

Thus pH = 7

Ex: Strong Base – Strong Acid:

40.0 mL of 1.00 M NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

I	0.0250 mol	0.0400 mol	0	-
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	+0.0250 mol
F	0	0.0150 mol	0.0250 mol	0.0250 mol

[NaOH] = 0.0150 mol/0.0650 L = 0.231 M

Thus pH = 13.4

Predicting the pH of an Acid-Base Mixture:

Strong Base – Weak Acid

$$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O$$

Consider the titration of 25.0 mL of 1.00 M $HC_2H_3O_2$ with 1.00 M NaOH. Calculate the pH on the addition of 10.0 mL, 25.0 mL, and 40.0 mL of the NaOH solution.

Ex: Strong Base – Weak Acid:

10.0 mL of 1.00 M NaOH:

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

I	0.0250 mol	0.0100 mol	0	-
C	-0.0100 mol	-0.0100 mol	+0.0100 mol	+0.0100 mol
F	0.0150 mol	0	0.0100 mol	0.0100 mol

System a Buffer!!

Thus pH = 4.56

Ex: Strong Base – Weak Acid:

25.0 mL of 1.00 M NaOH:

$$HC_2H_3O_2 + \quad NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

I	0.0250 mol	0.0250 mol	0	-
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	+0.0250 mol
F	0	0	0.0250 mol	0.0250 mol

System only contains a weak base and water. pH determined by weak base.

Ex: Strong Base – Weak Acid cont…:

$[C_2H_3O_2^-]$ = 0.0250 mol/0.0500 L = 0.500 M

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

I	0.500 M	-	0	-
C	-X		+X	+X
E	0.500-X		X	X

$$K_B = 5.56\times10^{-10} = \frac{X\cdot X}{0.500 - X}$$

X = $[OH^-]$ = 1.67×10^{-5} M, thus pH = 9.22

Ex: Strong Base – Weak Acid:

40.0 mL of 1.00 M NaOH:

$$HC_2H_3O_2 + \quad NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

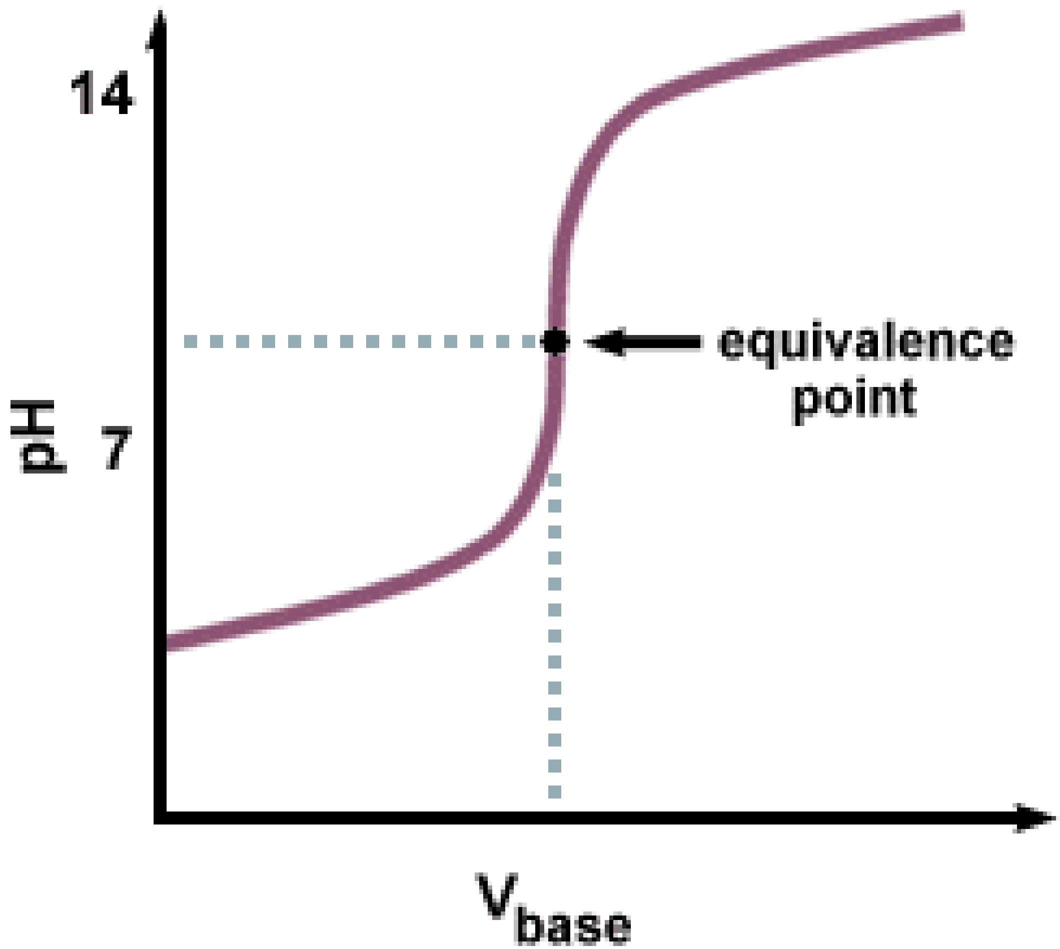
I	0.0250 mol	0.0400 mol	0	-
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	+0.0250 mol
F	0	0.0150 mol	0.0250 mol	0.0250 mol

[NaOH] = 0.0150 mol/0.0650 L = 0.231 M

Thus pH = 13.4

Acid-Base Indicators:

During acid base titration pH changes abruptly at equivalence point.



Acid-Base Indicators:

An acid base indicator is a weak acid whose color depends on the pH of the solution.

HIn: weak acid(acid color)

In^-: conjugate base(basic color)

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

Acid color **Base Color**

Acid-Base Indicators cont…:

$$pH = pK_{HIn} + Log\frac{[In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} > 10$$

$$\frac{[In^-]}{[HIn]} < 0.1$$

Base Color

Acid color

Some Indicators:

Indicator	Acid Color	Base Color	pH Range
phenolphthalien	clear	red	8-10
bromophenol blue	yellw	blue	3-4.5
Methyl Orange	red	yellw	3-5

Ex:

The indicator methyl red has a pK_{HIn} of 4.95. If the indicator is placed in a solution with a pH = 4.74, is it in the acid or base form?

Solubility Equilibria:

Solubility equilibria centres on the study of heterogeneous systems.

An aqueous solution containing aqueous NaCl and solid NaCl contains the following equilibrium.

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Na^+(aq)][Cl^-(aq)]$$

This equilibrium is described by the equilibrium constant, K_{sp}(solubility product).

Examples:

Ex:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$$

$$K_{sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2$$

Ex:2

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

$$K_{sp} = [Bi^{3+}(aq)]^2[S^{2-}(aq)]^3$$

Ex:3

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^{-}(aq)$$

$$K_{sp} = [Hg_2^{2+}(aq)][Cl^{-}(aq)]^2$$

K_{sp} and Solubility:

<u>solubility</u> – Concentration of a saturated solution.

Denoted by "s".

If we know the solubility we can calculate K_{sp} and likewise given K_{sp} we can calculate the solubility.

Examples:

Ex:

Silver chloride has a solubility of 1.31×10^{-5} M. Calculate K_{sp}.

Ex:2

Calculate the solubility of PbI_2.

$K_{sp}= 7.1\times10^{-9}$

Common-Ion Effect and Solubility

The solubility of a slightly soluble solute is decreased in the presence of a common ion.

Consider PbI_2 in the presence of KI.

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

PbI_2 ppt out

$[Pb^{2+}(aq)]$ decreases

$[I^-(aq)]$ is greater

Examples:

Ex:3

What is the solubility of PbI_2 in 0.10 M KI?

$K_{sp} = 7.1\times10^{-9}$

Reaction Quotient(Q):

Used to determine if a solution is dilute, saturated, or supersaturated.

$Q = K_{sp}$	saturated
$Q < K_{sp}$	unsaturated
$Q > K_{sp}$	supersaturated (ppt occurs)

Reaction Quotient(Q) cont…:

Ex:
If $AgNO_3$ and KI are mixed to obtain a solution with $[Ag^+(aq)]$ = 0.010 M and $[I^-(aq)]$ = 0.015 M, is the solution unsaturated, saturated, or supersaturated?
$K_{sp}(AgI) = 8.5\times10^{-17}$