# Aqueous Equilibrium

# Buffers

Acid or Base



Buffer

⟹ pH  stays constant.
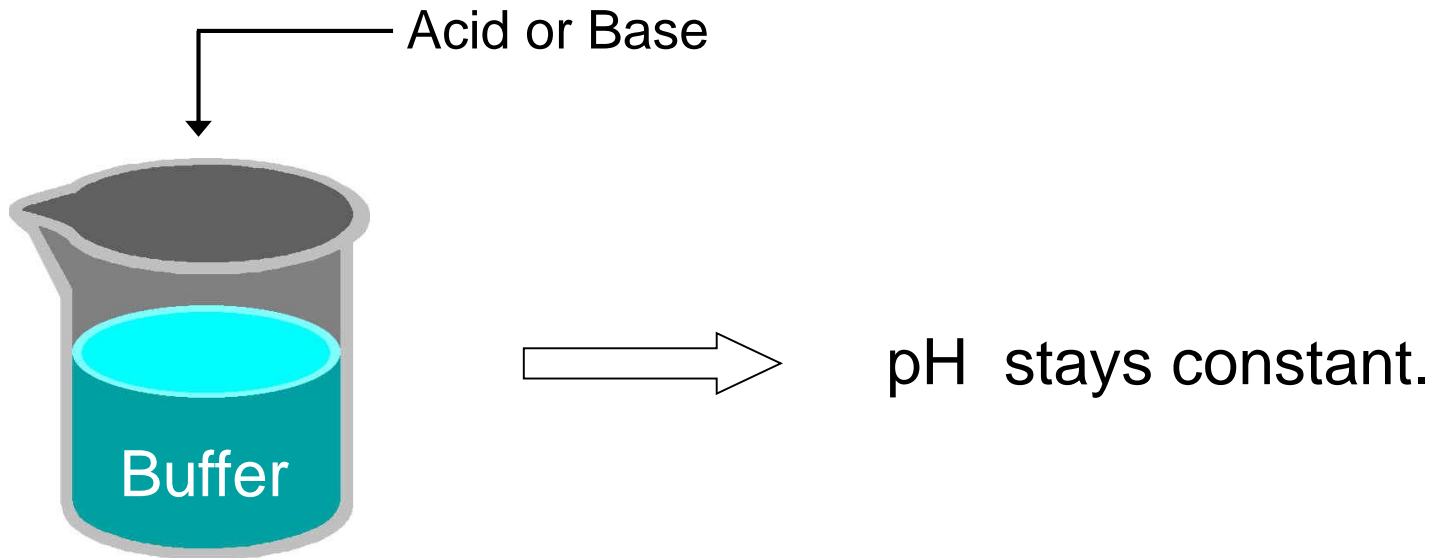
A buffer resists changes in pH when limited amounts of acid or base are added.

# Buffers

Our blood is a buffer solution.

Acid

Acid

Base

Base

pH of blood ≈ 7.4

Shock Absorber

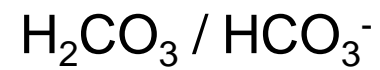# Buffers

Ocean is a buffer solution.
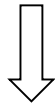


pH ≈ 8

Carbonate buffer $H_2CO_3$ / $HCO_3^-$
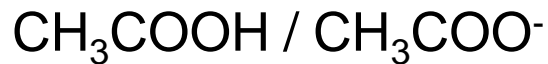
# Buffer Composition

Weak Acid + its Conjugate base (in equilibrium)

⇩

salt of the weak acid

$CH_3COOH + CH_3COO^-Na^+$

$CH_3COOH / CH_3COO^-$
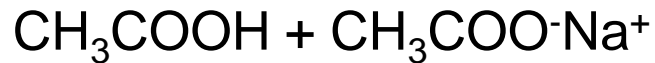
Or it can be weak base with it's conjugate acid.

# Buffers in our body

pH of blood = between 7.35 and 7.45
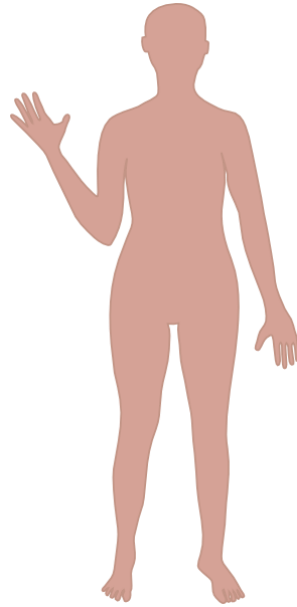
| | | |
|---|---|---|
| Carbonate buffer | $H_2CO_3$ / $HCO_3^-$ |
| Phosphate buffer | $H_2PO_4^-$ / $HPO_4^{2-}$ |
| Proteins buffer | |

# How do buffers work?

Carbonate buffer $\quad\quad\quad H_2CO_3 \,/\, HCO_3^-$
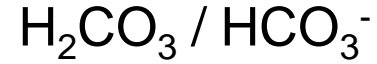
If we eat an acidic food:

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$$
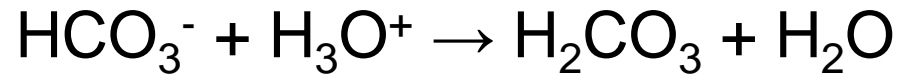
If we eat a basic food:

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$
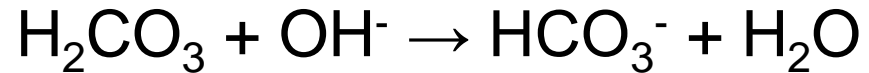
# How to design a Buffer

We will calculate our **initial buffer pH**

(an acid and it's conjugate base).

**Practice 1:** Suppose we culture bacteria, something close to a pH = 4. We prepare a buffer solution that is 0.040 M $NaCH_3CO_2$ (aq) and 0.080 M $CH_3COOH$(aq) at 25°C. What is the pH of the buffer solution ?

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + CH_3COO^- (aq), K_a = 1.8 \times 10^{-5}$$
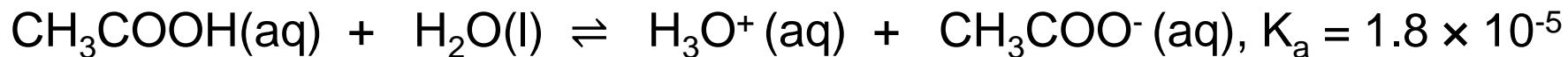
We can make an ICE table, with our known values first,

|  | $CH_3COOH$ | $H_3O^+$ | $CH_3COO^-$ |
|---|---|---|---|
| initial | 0.080 | 0 | 0.040 |
| change | −x | +x | +x |
| equilibrium | 0.080 -x | x | 0.040 + x |

For a quick approximation $K_a \times 100 < 0.040$ (0.040 is the smallest of the two starting concentrations), so we ignore -x, and +x, we'll still check it at the end for 5% ionization to make sure.

|  | CH$_3$COOH | H$_3$O$^+$ | CH$_3$COO$^-$ |
|---|---|---|---|
| initial | 0.080 | 0 | 0.040 |
| change | $-x$ | $+x$ | $+x$ |
| equilibrium | 0.080 | x | 0.040 |

Solving $K_a$ = $1.8 \times 10^{-5}$ = $\dfrac{(0.040)\,x}{0.080}$

$x = \dfrac{(1.8 \times 10^{-5})\, 0.080}{0.040}$

$x = 3.6 \times 10^{-5}$ = [H$_3$O$^+$], using pH = -log [H$_3$O$^+$]

pH = -log [$3.6 \times 10^{-5}$] = 4.44

percentage deprotonation = $\dfrac{3.6 \times 10^{-5}}{0.040}$ × 100 = 0.09%  (which is less than 5% 👍)

**Practice 2:** Calculate the pH of a buffer solution that is 0.040 M $NH_4Cl(aq)$ and 0.030 M $NH_3(aq)$.

In this case we can write it out either as an acid given the $K_a$ or as a base given the $K_b$. We'll treat this as an acid, and look up the $K_a$,

$$NH_4^+ (aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + NH_3(aq), \quad K_a = 5.6 \times 10^{-10}$$

We can make an ICE table, with our known concentrations first,

|  | $NH_4^+$ | $H_3O^+$ | $NH_3$ |
|---|---|---|---|
| initial | 0.040 | 0 | 0.030 |
| change | $-x$ | $+ x$ | $+ x$ |
| equilibrium | 0.040 - x | x | 0.030 + x |

For a quick approximation $K_a \times 100 < 0.030$, so we ignore -x, and +x, we'll still check it at the end for 5% ionization to make sure.

|  | $NH_4^+$ | $H_3O^+$ | $NH_3$ |
|---|---|---|---|
| initial | 0.040 | 0 | 0.030 |
| change | −x | + x | + x |
| equilibrium | 0.040 | x | 0.030 |

Solving $K_a = 5.6 \times 10^{-10} = \dfrac{(0.030)\,x}{0.040}$

$x = \dfrac{(5.6 \times 10^{-10})\,0.040}{0.030}$

$x = 7.5 \times 10^{-10} = [H_3O^+]$, using pH = -log $[H_3O^+]$

pH = -log $[7.5 \times 10^{-10}] = 9.13$

percentage deprotonation = $\dfrac{7.5 \times 10^{-10}}{0.030} \times 100 = 3 \times 10^{-6}$ %  (which is less than 5% 👍)

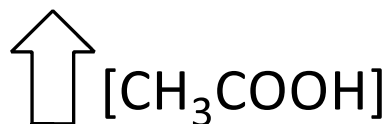**Practice 3:** If we add 1 mL of 1.0 HCl solution to 1.0 L of water with the pH of 7.0, calculate the new pH?

Adding 1 mL of 1.0 M HCl solution, using our dilution formula ($M_1V_1 = M_2V_2$), and assuming 1 mL would not change the volume of 1.0 L significantly, 0.001L,

$$M_2 = \frac{M_1V_1}{V_2}, \quad \frac{1.0\ M \times 0.001L}{1.0\ L} = 0.001\ M\ H_3O^+, \quad pH = -\log(0.001) = 3.0$$

That means the $\Delta pH = 7 - 3 = 4$.      It is not much resistance.

So the effect of 1 mL of a strong acid on 1 L of pure water (1 part per 1000) can increase water's ion concentration [$H_3O^+$] by 10,000!

If we add 1 mL of 1.0M HCl to a buffer solution:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

①

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

②

$$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

⇧ $[CH_3COOH]$      $[H_3O^+]$ ⇩      $[CH_3COO^-]$ ⇩
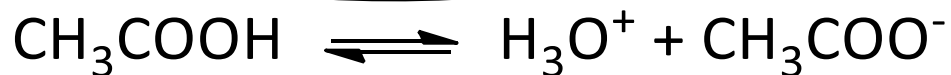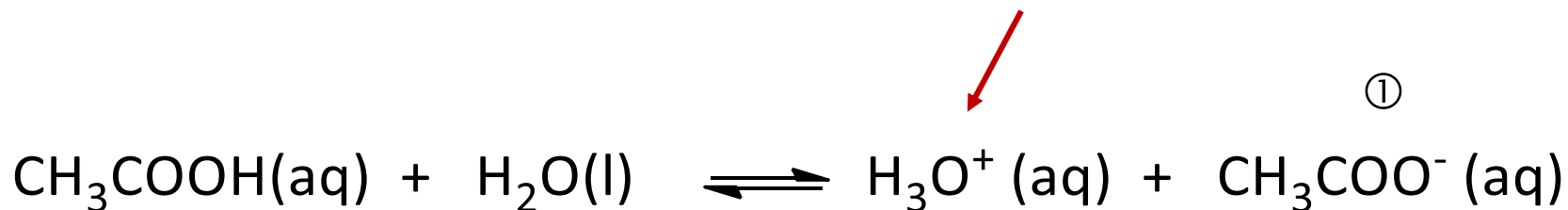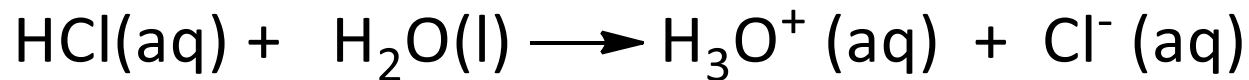
③
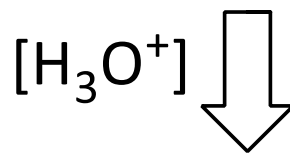
HCl is removed, and replaced with $CH_3COOH$!

1. The $H_3O^+$ from the HCl reacts with the $CH_3COO^-$ ;
2. This produces more acid, $CH_3COOH$;
3. The effect is a strong acid is removed, **Replaced** with a weak acid.

Remember that a **strong acid** reacts <u>**completely**</u> with a **weak base**.
**Practice 4:** Adding 1 mL of 1.0 M HCl solution to, a 1.0 L buffer solution of 0.040 M NaCH$_3$CO$_2$ (aq) and 0.080 M CH$_3$COOH(aq). Find the pH.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + CH_3COO^- (aq), \quad K_a = 1.8 \times 10^{-5}$$

**H$_3$O$^+$ + CH$_3$COO$^-$ $\rightleftharpoons$ CH$_3$COOH** Acid reacts with the base first.

The ICE table shows the reaction between the strong acid and weak base- these must be in <u>**moles**</u> since we're showing a reaction.

$$M = \frac{n \ (mol)}{V \ (L)} \rightarrow 1.0 \ M \ HCl = \frac{n}{0.001 \ L} \rightarrow n = 0.001 \ mol \ HCl$$

$$M = \frac{n \ (mol)}{V \ (L)} \rightarrow 0.040 \ M \ CH_3COO^- = \frac{n}{1.0 \ L} \rightarrow n = 0.040 \ mol \ CH_3COO^-$$

|  | CH$_3$COO$^-$ | H$_3$O$^+$ | CH$_3$COOH |
|---|---|---|---|
| initial | 0.040 mol | 0.001 mol | 0.080 mol |
| change | -0.001 mol | -0.001 mol | +0.001 mol |
| equilibrium | 0.039 mol | 0 | 0.081 mol |

| | $CH_3COO^-$ | $H_3O^+$ | $CH_3COOH$ |
|---|---|---|---|
| initial | 0.040 mol | 0.001 mol | 0.080 mol |
| change | -0.001 mol | -0.001 mol | +0.001 mol |
| equilibrium | 0.039 mol | 0 | 0.081 mol |

0.039 mol in 1 L = 0.039 mol·L$^{-1}$

0.081 mol in 1 L = 0.081 mol·L$^{-1}$

We use these new values to calculate the pH of the buffer, after the HCl was added.

| | $CH_3COOH$ | $H_3O^+$ | $CH_3COO^-$ |
|---|---|---|---|
| initial | 0.081 | 0 | 0.039 |
| change | $-x$ | $+x$ | $+x$ |
| equilibrium | 0.081 - x | x | 0.039 + x |

Solving $K_a$ = $1.8 \times 10^{-5}$ = $\dfrac{(0.039)\ x}{0.081}$ , $x = 3.7 \times 10^{-5} = [H_3O^+]$

using pH = -log $[H_3O^+]$ , pH = -log $[3.7 \times 10^{-5}]$ = 4.43
ΔpH = 4.44 - 4.43 = 0.01, that is a much <span style="color:magenta">less dramatic</span> increase then the 10,000 times increase without a buffer in pure water. <span style="color:purple">Also</span>, the Strong Acid is **gone**, replaced with a Weak Acid.

If we add 1 mL of 1.0M NaOH to a buffer solution:

$$NaOH(aq) \longrightarrow OH^-(aq) + Na^+(aq)$$

① $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

② $OH^- + CH_3COOH \rightleftharpoons CH_3COO^-$
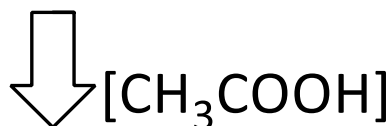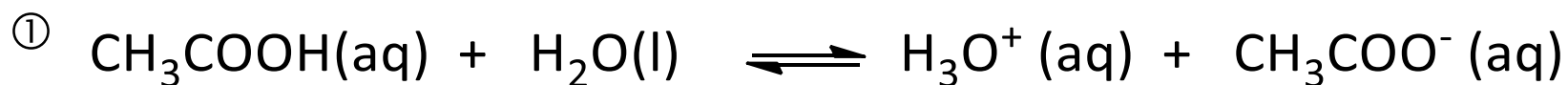
⬇ $[CH_3COOH]$          $[CH_3COO^-]$ ⬆ ③

NaOH is removed, and replaced with $CH_3COO^-$!

1. The $OH^-$ from the NaOH reacts with the $CH_3COOH$ ;
2. This produces more conjugate base, $CH_3COO^-$;
3. What happened, is a strong base is **Replaced** with a weak base.

**Practice 5:** Adding 1.2 g NaOH (0.030 mol) to 500. mL of a buffer solution that is 0.040 M $NaCH_3CO_2$(aq) and 0.080 M $CH_3COOH$(aq). Find the pH:

$$OH^- + CH_3COOH \rightleftharpoons CH_3COO^-$$

We setup an ICE table that shows the reaction between the strong base and weak acid-these must be in **moles** since we're showing a reaction.

$$M = \frac{n \, (mol)}{V \, (L)} \rightarrow 0.080 \, M \, CH_3COOH = \frac{n}{0.500 \, L} \rightarrow n = 0.040 \, mol \, CH_3COOH$$

$$M = \frac{n \, (mol)}{V \, (L)} \rightarrow 0.040 \, M \, CH_3COO^- = \frac{n}{0.500 \, L} \rightarrow n = 0.020 \, mol \, CH_3COO^-$$

|  | $CH_3COOH$ | $OH^-$ | $CH_3COO^-$ |
|---|---|---|---|
| initial | 0.040 mol | 0.030 mol | 0.020 mol |
| change | -0.030 mol | -0.030 mol | +0.030 mol |
| equilibrium | 0.010 mol | 0 | 0.050 mol |

Convert moles to molarity.

$$M = \frac{n\ (mol)}{V\ (L)} = \frac{0.010\ mol\ acid}{0.500\ L} = 0.020\ M\ acid$$

| | CH$_3$COOH | OH$^-$ | CH$_3$COO$^-$ |
|---|---|---|---|
| initial | 0.040 mol | 0.030 mol | 0.020 mol |
| change | -0.030 mol | -0.030 mol | +0.030 mol |
| equilibrium | 0.010 mol | 0 | 0.050 mol |

$$M = \frac{n\ (mol)}{V\ (L)} = \frac{0.050\ mol\ aceate}{0.500\ L} = 0.10\ M\ acetate$$

Recalculate the new pH.

| | CH$_3$COOH | H$_3$O$^+$ | CH$_3$COO$^-$ |
|---|---|---|---|
| initial | 0.020 | 0 | 0.10 |
| change | $-x$ | $+x$ | $+x$ |
| equilibrium | 0.020 - x | x | 0.10 + x |

Solving $K_a = 1.8 \times 10^{-5} = \frac{(0.10)\ x}{0.020}$ , $x = 3.6 \times 10^{-6} = [H_3O^+]$

using pH = -log [H$_3$O$^+$] , pH = -log [3.6 × 10$^{-6}$] = 5.44
ΔpH = 5.44 - 4.44 = 1.0  which is a much less dramatic increase in pure water from 12.78 – 7.00 = 5.78 pH increase. And the strong base is gone, leaving only the weak base.

# To prepare a buffer match the pH to the $pK_a$ or pOH to the $pK_b$

Typically, a buffer is made of equal concentrations of both the conjugate acid and base, this is called **equimolar**.

Since $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + A^- (aq)$ and being equimolar in conjugate acid base, $[HA] = [A^-]$,

Then $[H_3O^+] = K_a$, which means $\boxed{pH = pK_a}$

For example, if you wanted a buffer solution close to a pH of 5 you would choose the acetic/acetate buffer.

| Acid Buffer | pKa |
|-------------|------|
| $HC_2H_3O_2/C_2H_3O_2^-$ | 4.75 |
| $HNO_2/NO_2^-$ | 3.37 |
| $HClO_2/ClO_2^-$ | 2.00 |

# Quick pH buffer approximations: Henderson-Hasselbalch

For any weak acid $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + A^- (aq)$

$K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ the equation is rearranged into $[H_3O^+] = K_a \dfrac{[HA]}{[A^-]}$

From $\log x - \log (1/x)$,

Henderson-Hasselbalch: $pH = pKa + \log \dfrac{[base]_{intial}}{[Acid]_{intial}}$

**Practice 6:** Calculate the ratio of the molarities of $CO_3^{2-}$ and $HCO_3^-$ ions required to achieve buffering at pH = 9.50. The $pK_{a2}$ of $H_2CO_3$ is 10.25.

Using the Henderson-Hasselbalch form:    $pH = pKa + \log \dfrac{[base]_{intial}}{[Acid]_{intial}}$

$9.50 = 10.25 + \log \dfrac{[CO_3^{2-}]}{[HCO_3^-]}$

$\log \dfrac{[CO_3^{2-}]}{[HCO_3^-]} = 9.50 - 10.25 = -0.75$  take $10^x$ (antilog) of both sides

$\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{-0.75} = 0.18$,  this is the ratio or also written as $\dfrac{0.18}{1}$

Which means $[CO_3^{2-}] = 0.18$ M ,and $[HCO_3^-] = 1.00$ M

# Buffer Capacity

Just as a sponge can hold only so much water, a buffer can mop up only so many hydronium ions.

**Buffer capacity** is the maximum amount of acid or base that can be added before the buffer loses its ability to resist large changes in pH.

Adding excess acid will overwhelm the conjugate base, or adding to much excess base will overwhelm the conjugate acid.

Broadly speaking, a buffer is found experimentally to have a high capacity for acid when the amount of base present is at least 10% of the amount of acid; similarly for a base.

# Buffer Capacity

Experimentally, a buffer works best when it is $\pm$ 1 pH range of the $pK_a$ of the buffer solution.

Blood plasma, with $HCO_3^-$ ions is about 20 times that of $H_2CO_3$, seems to be outside the range for optimum buffering.
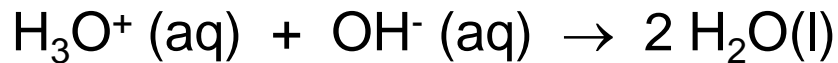


However, the principal waste products cells are carboxylic acids, such as lactic acid.

# Strong Acid-Strong Base Titrations

In a neutralization reaction a strong acid mixes with a strong base,

$$H_3O^+ (aq) + OH^- (aq) \rightarrow 2\,H_2O(l)$$

A plot of the pH against the volume of titrant added during a titration is called a **pH curve**.

A strong acid/base titration shows at the stoichiometric point a sudden change in pH near 7
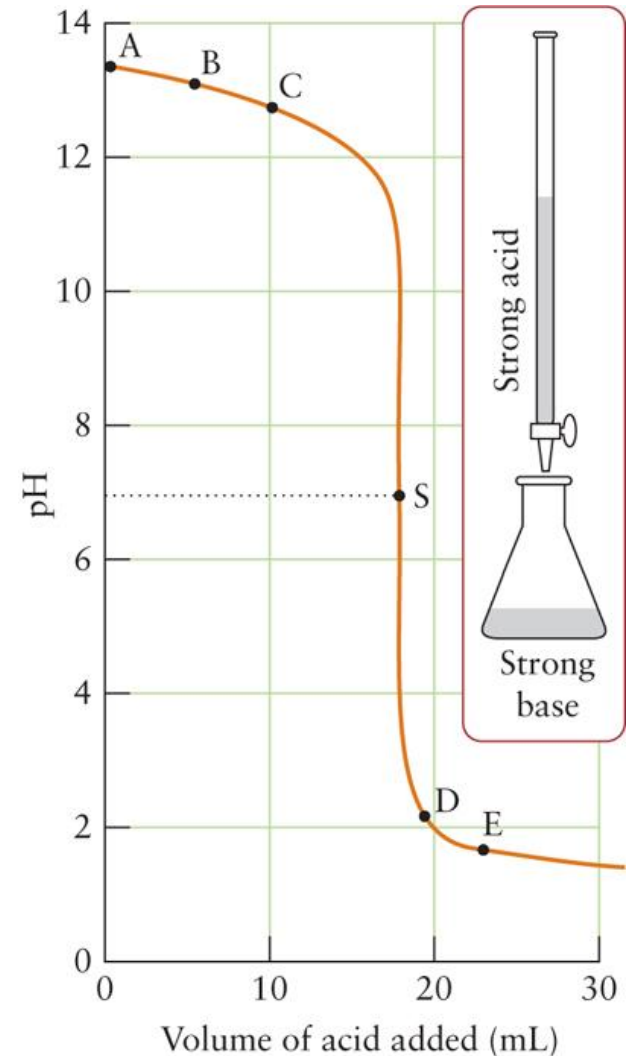
# Strong Acid-Strong Base Titrations: Calculations

- Determine the **moles** of acid or base needed;

- Write the neutralization reaction;

- Calculate the **final concentration** by taking the **moles** calculated divided by the **total volume** (total volume = volume analyte + volume titrant)

**Practice 7:** Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq) and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant we can expect the pH to decrease slightly from its initial value. Calculate the new pH.

Initial $[OH^-]$ = 0.250M, pOH = -log 0.250 = 0.602, pH = 14 - .0602 = 13.40

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

$\uparrow H_3O^+$ (aq)  +  $\downarrow OH^-$ (aq)  $\rightarrow$  2 $H_2O$(l) $\uparrow$
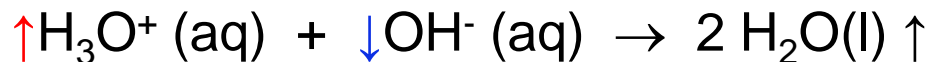
Le Chatelier's principle say an **increase** in acid will cause a **shift** to the reactant side, thereby **removing** base, so the pH will decrease.

**Practice 7:** Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq) and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant we can expect the pH to decrease slightly from its initial value. Calculate the new pH.

Initial OH⁻ mole:      $M = \dfrac{n \, (mol)}{V \, (L)} \rightarrow 0.250 \text{ M NaOH} = \dfrac{n}{0.02500 \text{ L}} \rightarrow n = 0.0063 \text{ mol NaOH}$

Moles $H_3O^+$ added:      $M = \dfrac{n \, (mol)}{V \, (L)} \rightarrow 0.340 \text{ M HCl} = \dfrac{n}{0.00500 \text{ L}} \rightarrow n = 0.0017 \text{ mol } H_3O^+$

A strong acid will react completely with a strong base or
0.0063 mol OH⁻ - 0.0017 mol $H_3O^+$ = 0.0046 mol OH⁻ remain.

The new volume is 25.00 mL of basic solution +  5.00 mL of $H_3O^+$ = 30.00 mL or 0.03000 L total.

New concentration of [OH⁻] = $\dfrac{0.0046 \text{ molOH}^-}{0.03000 \text{ L OH}^-}$ = 0.152 M or pOH = 0.82

pH  +  pOH = 14,  so pH = 13.18  and ΔpH = 13.40 − 13.18 = 0.22

# Strong Acid-Strong Base Titrations: Overview

In the titration of a strong acids with strong bases, the pH changes slowly, then rapidly through pH = 7 at the stoichiometric point, and slowly again.
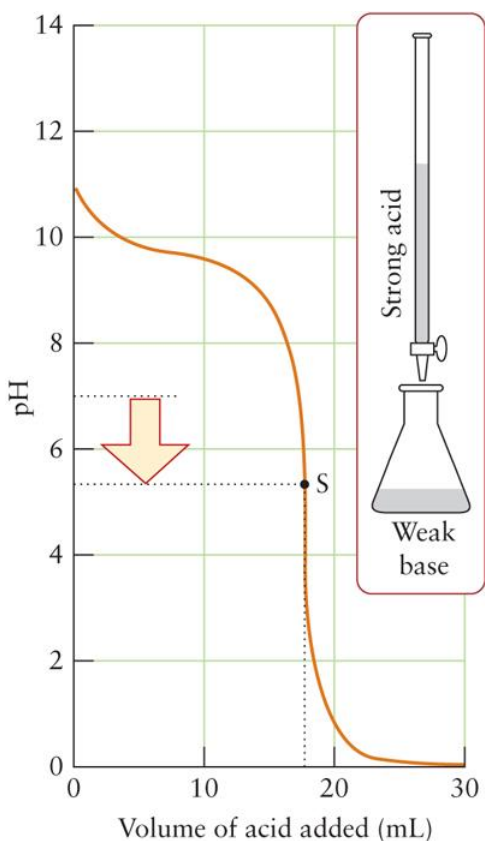
Stoichiometric point (Equivalence point):

$$[H_3O^+] = [OH^-]$$
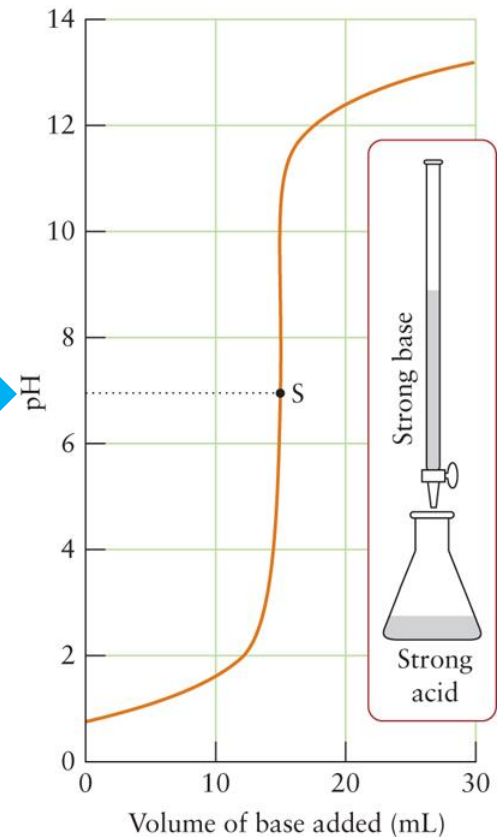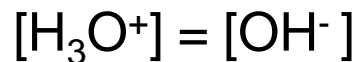


A final pH of 7 is reached for all strong acid strong base.

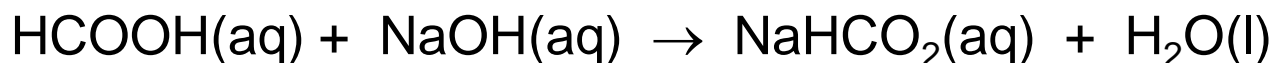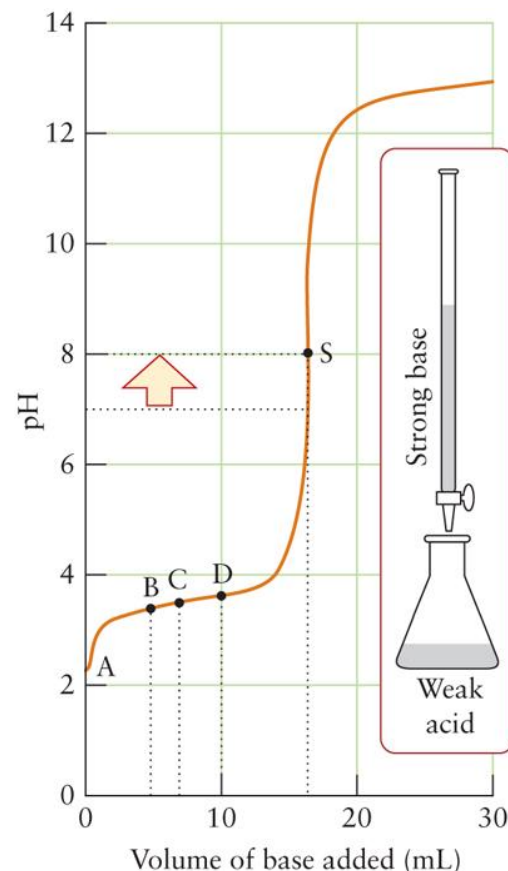# Strong Acid-Weak Base and Weak Acid-Strong Base Titrations

A more common titration is between a **weak** acid or base and a **strong** base or acid.



The pH in this case will not be 7.

The pH depends on the conjugate salt produced.

In the next example we calculate the pH of this solution.

$$HCOOH(aq) + NaOH(aq) \rightarrow NaHCO_2(aq) + H_2O(l)$$

# Estimating the pH at the stoichiometric point of the titration of a weak acid with a strong base

**Practice 8:** Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M HCOOH(aq) with 0.150 M NaOH(aq).

The stoichiometric point only has $Na^+$ (aq) and $HCO_2^-$ (aq).

$$HCOOH(aq) + NaOH(aq) \rightarrow NaHCO_2(aq) + H_2O(l)$$
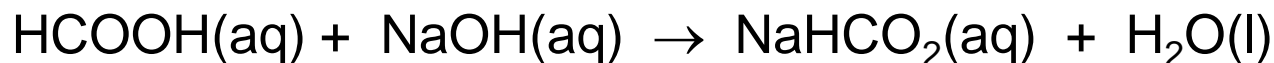
This is a 2 part problem

-first, find the moles $HCO_2^-$ produced and liters of NaOH needed,

-second, calculate the pH of the new conjugate base produced.

$$HCO_2^- (aq) + H_2O(l) \rightleftharpoons OH^- (aq) + HCOOH(aq)$$

**Practice 8:** Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M HCOOH(aq) with 0.150 M NaOH(aq).

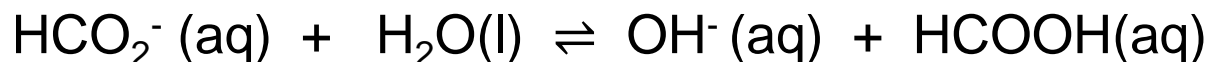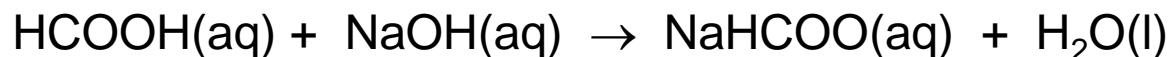HCOOH(aq) + NaOH(aq) → NaHCOO(aq) + H$_2$O(l)

The NIE is:   HCOOH(aq) + OH$^-$(aq) → HCOO$^-$(aq) + H$_2$O(l)

First, find the moles of HCOOH, this will help us calculate the volume of NaOH needed.

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}} \rightarrow 0.100 \text{ M HCOOH} = \frac{n}{0.02500 \text{ L}} \rightarrow n = 0.002500 \text{ mol HCOOH}$$

$$0.002500 \text{ mol HCOOH} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol COOH}} \rightarrow n = 0.002500 \text{ mol NaOH}$$

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}} \rightarrow 0.150 \text{ M NaOH} = \frac{0.002500 \text{ mol NaOH}}{V \text{ (L)}} \rightarrow V = 0.0167 \text{ L NaOH}$$

Total volume is .02500 L + 0.0167 L = 0.0417 L

$$\text{Molarity of HCOO}^- = \frac{0.002500 \text{ mol}}{0.0417 \text{ L}} = 0.0600 \text{ M HCOO}^-$$

**Practice 8:** Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M HCOOH(aq) with 0.150 M NaOH(aq).

In the second step we look at the new equilibrium of the **conjugate base**,
**HCOO⁻** (aq)  +  $H_2O$(l)  ⇌  OH⁻ (aq)  +  HCOOH(aq)

The $K_a$ = 1.8 × 10⁻⁴, so the $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$

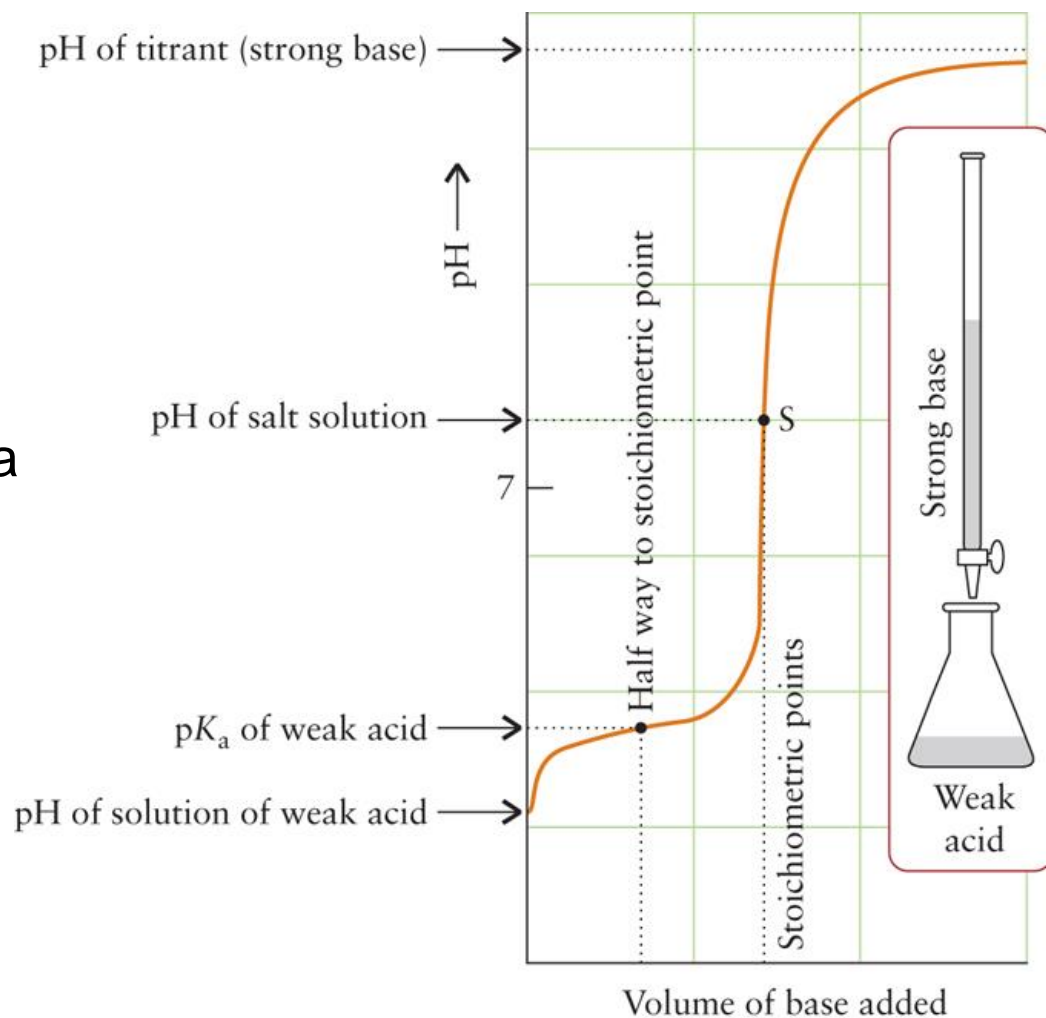|  | HCOO⁻ | OH⁻ | HCOOH |
|---|---|---|---|
| initial | 0. 0060 | 0 | 0 |
| change | - x | + x | + x |
| equilibrium | 0.0600 | x | x |

Solving $K_b = 5.6 \times 10^{-11} = \dfrac{x^2}{0.0600}$ ,  $x = 1.8 \times 10^{-6} = [OH^-]$

pOH = -log [1.8 × 10⁻⁶ ] = 5.74, pH = 14 - 5.74 = 8.26

percentage deprotonation = $\dfrac{1.8 \times 10^{-6}}{0.0600} \times 100 = 0.003\,\%$

# Calculating the pH during a titration

At the halfway to stoichiometric points, [HA] = [A⁻] and pH = $pK_a$. The flatness of the curve near pH = $pK_a$ illustrates the ability of a buffer solution to stabilize the pH of the solution.

pH of titrant (strong base) →

pH ↑

Half way to stoichiometric point

pH of salt solution →

7

$pK_a$ of weak acid →

pH of solution of weak acid →

Stoichiometric points

Strong base

Weak acid

S

Volume of base added

The slow change in pH about halfway to the stoichiometric point indicates that the solution acts as a buffer in that region

# Calculating the pH before the stoichiometric point in a weak acid-strong base titration

**Practice 9:** Calculate the pH of (a) 0.100 M HCOOH(aq) and (b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid. Use $K_a = 1.8 \times 10^{-4}$ for HCOOH

In (a) we calculate the initial pH. Since HCOOH is a weak acid there will be both the acid and it's conjugate base so we make an ICE table to find pH;

In (b) we need to find the moles of NaOH that will react with HCOOH, which means $HCOO^-$ is formed, so a new pH is calculated.

**Practice 9:** Calculate the pH of (a) 0.100 M HCOOH(aq) and (b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid. Use $K_a = 1.8 \times 10^{-4}$ for HCOOH

(a) $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$
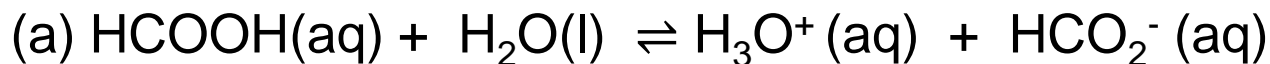
ICE table

|  | HCOOH | $H_3O^+$ | HCOO$^-$ |
|---|---|---|---|
| initial | 0.100 | 0 | 0 |
| change | - x | + x | + x |
| equilibrium | 0.100 | x | x |

$1.8 \times 10^{-4} = \dfrac{x^2}{0.100}$ , $x = 0.00424$

$pH = - \log [H_3O^+]$, $pH = - \log 0.00424 = 2.37$

(b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

We need to find the moles of base that react with the acid.

$$HCOOH(aq) + HO^-(aq) \rightleftharpoons H_2O(l) + HCOO^-(aq)$$
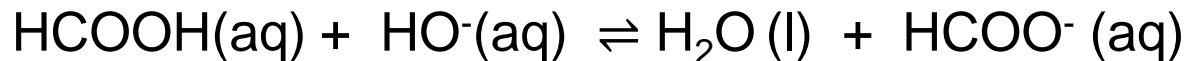
$$M = \frac{n\ (mol)}{V\ (L)} \rightarrow 0.150\ M\ NaOH = \frac{n}{0.00500\ L} \rightarrow n = 0.000750\ mol\ OH^-$$

$$= 0.000750\ mol\ HCOO^-$$

$$M = \frac{n\ (mol)}{V\ (L)} \rightarrow 0.100\ M\ HCOOH = \frac{n}{0.0250\ L} \rightarrow n = 0.0025\ mol\ HCOOH$$

Strong base is used **completely**:

0.0025 mol − 0.0000750 mol = 0.00175 mol HCOOH remains

(b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$
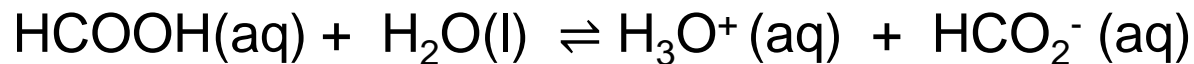
New volume is 25.00 + 5.00 mL = 30.00 mL or 0.030 L

$$[HCOOH] = \frac{0.00175 \text{ mol}}{0.030 \text{ L}} = 0.0583 \text{ M}$$

$$[HCOO^-] = \frac{0.000750 \text{ mol}}{0.030 \text{ L}} = 0.0250 \text{ M}$$

$$pH = pKa + \log \frac{[\text{base}]_{intial}}{[\text{Acid}]_{intial}}$$

$$pH = 3.75 + \log \frac{0.0250}{0.0583} = 3.38$$

# Solubility Equilibria

A saturated solution is an equilibrium system.

# of solute dissolved = # of solute precipitated

Solubility is an equilibrium position.

Ions will collide in a solution and re-form the solid.

# Solubility Equilibria

Our **goal** is to <u>control the formation of precipitates</u>.

These common methods in the laboratory to separate and analyze mixtures of salts. They also have important practical applications in municipal **wastewater treatment**, the **extraction of minerals from seawater**, the **formation and loss of bones and teeth**, and the **global carbon cycle**.

# Solubility Equilibria

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
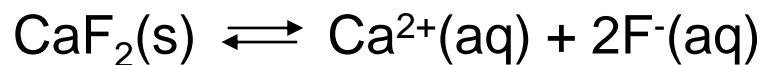
At equilibrium:

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

Solubility Product Constant (Solubility Product)

$CaF_2$ is a pure solid and it is not included.

Amount of excess solid present does not affect the position of the solubility equilibrium.

# Solubility Equilibria

**Practice 7:** $K_{sp}$ of solid $AgI(s)$ is $1.5\times10^{-16}$ at 25°C. Calculate the solubility of $AgI(s)$ in water at 25°C.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

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

x mol/L $AgI(s) \rightleftharpoons$ x mol/L $Ag^+(aq)$ + x mol/L $I^-(aq)$

$[Ag^+]$ = x mol/L
$[I^-]$ = x mol/L

$$K_{sp} = 1.5\times10^{-16} = (x)(x) = x^2$$

$$x = \sqrt{1.5\times10^{-16}} = 1.2\times10^{-8} \text{ mol/L} \qquad \text{Solubility of AgI}$$

**Practice 8:** The molar solubility of silver bromide, AgBr, at 25°C is $8.8 \times 10^{-7}$ mol·L$^{-1}$. What is the value of $K_{sp}$ for silver bromide?

First, we write the equilibrium expression for the solubility product.

$$AgBr(s) \rightleftharpoons Ag^+ (aq) + Br^-(aq)$$

Write the expression for the solubility product.

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

Using the **first** method, since the mole ratios are 1:1 we solve, for $K_{sp}$, $K_{sp} = [Ag^+][Br^-]$, where both $[Ag^+]$, $[Br^-] = x$, $K_{sp} = x^2$,

$x = 8.8 \times 10^{-7}$ mol·L$^{-1}$, so $K_{sp} = (8.8 \times 10^{-7})^2 = 7.7 \times 10^{-13}$

**Practice 8:** The molar solubility of silver bromide, AgBr, at 25°C is $8.8 \times 10^{-7}$ mol·L$^{-1}$. What is the value of $K_{sp}$ for silver bromide?

$$AgBr(s) \rightleftharpoons Ag^+ (aq) + Br^-(aq) \qquad K_{sp} = [Ag^+][Br^-]$$

The **second** method uses an ICE table

|             | AgBr | $Ag^+$ | $Br^-$ |
|-------------|------|--------|--------|
| initial     | N/A  | 0      | 0      |
| change      |      | $+ x$  | $+ x$  |
| equilibrium |      | $x$    | $x$    |

From $K_{sp} = [Ag^+][Br^-]$, $K_{sp} = x^2$, $x = 8.8 \times 10^{-7}$ mol·L$^{-1}$

so $K_{sp} = (8.8 \times 10^{-7})^2 = 7.7 \times 10^{-13}$

# The Common-Ion Effect

Making precipitates of sparingly soluble salt, like heavy metal ions such as **lead** and **mercury** can be removed from municipal waste water by precipitating them as the **hydroxides**.

How can we remove these ions heavy metal ions from solution?

Le Chatelier's principle tells us that, if we add a second salt or an acid, the same ions-a "common ion"- that the equilibrium shift away from the added ion.

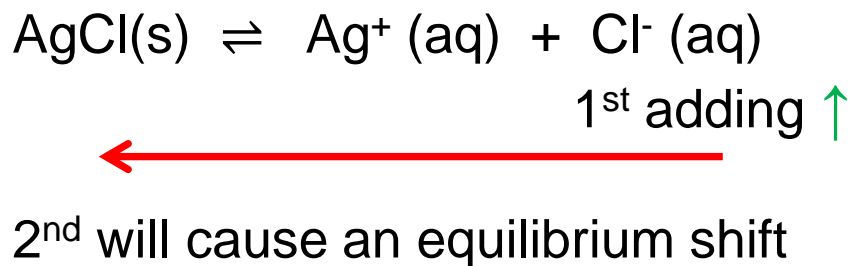The idea being we can precipitate unwanted ions using the **common-ion effect**.

# The Common-Ion Effect

A quantitative understanding of the common-ion effect in practice is as follows with AgCl(s).

$AgCl(s) \rightleftharpoons Ag^+ (ag) + Cl^- (aq)$   $K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$.
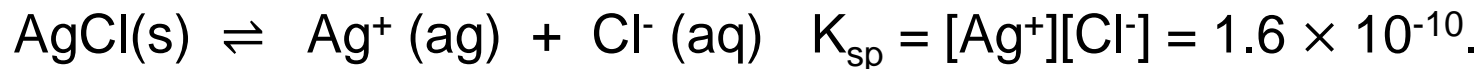
The molar solubility of AgCl in water is $1.3 \times 10^{-5}$ mol·L$^{-1}$.

According to Le Chatelier's principle, adding a common ion to this reaction **Cl$^-$**, in the form or **NaCl**, will have the effect of forming more **AgCl**(s),

$$AgCl(s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq)$$

1$^{st}$ adding ↑

⟵

2$^{nd}$ will cause an equilibrium shift

This will produce more ↑AgCl(s).

**Practice 9:** Estimating the effect of a common ion on solubility silver chloride in $1.0 \times 10^{-4}$ M NaCl(aq).
$K_{sp} = 1.6 \times 10^{-10}$.
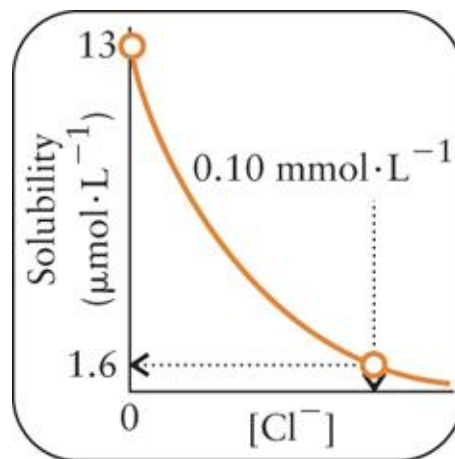
$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$, the molar solubility of AgCl in water before adding NaCl is $1.3 \times 10^{-5}$ mol·L$^{-1}$.

$$[Ag^+] = \frac{Ksp}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-4}} = 1.6 \times 10^{-6} \text{ which is 10 times less than}$$
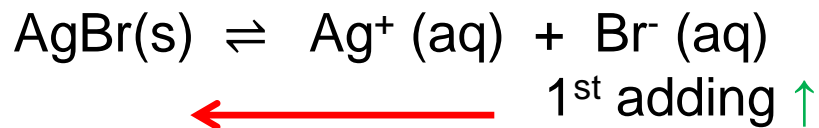"solubility" in pure water.

$$AgCl(s) \; \rightleftharpoons \; Ag^+ \, (ag) \; + \; Cl^- \, (aq)$$
$\longleftarrow$      1$^{st}$ adding ↑
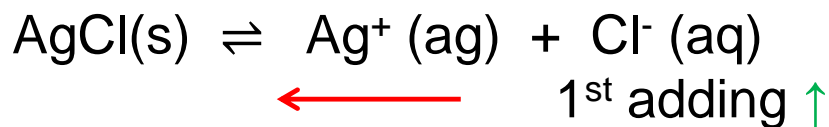
producing more ↑AgCl(s)

**Practice 10:** What is the approximate molar solubility of silver bromide in 0.10 M $CaBr_2$(aq)? $K_{sp} = [Ag^+][Br^-] = 7.7 \times 10^{-13}$.

$AgBr(s) \rightleftharpoons Ag^+ (aq) + Br^- (aq)$

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{.20} = 3.9 \times 10^{-12}$$

Adding Br-, shifts the equilibrium to make more AgBr(s)

$AgBr(s) \rightleftharpoons Ag^+ (aq) + Br^- (aq)$

$\longleftarrow$     1st adding ↑

producing more ↑AgCl(s)

As a comparison, we can find the molar solubility of AgBr in water as $x^2 = 7.7 \times 10^{-13}$, $x = \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7}$ mol·L⁻¹. Now the decrease in $Ag^+$ ions is **10,000 times less** then pure water.

# Predicting Precipitation

In a multi-ion solution it is important to precipitate one ion at time.

It's an analytical idea-removing one ion at a time.

We gain insight as to how this works by calculating and comparing Q, the reaction quotient, to K, the equilibrium constant.

Here we use the equilibrium constant is the solubility product, $K_{sp}$, and the reaction quotient is denoted $Q_{sp}$

Precipitation occurs when $Q_{sp}$ is **greater** than $K_{sp}$.
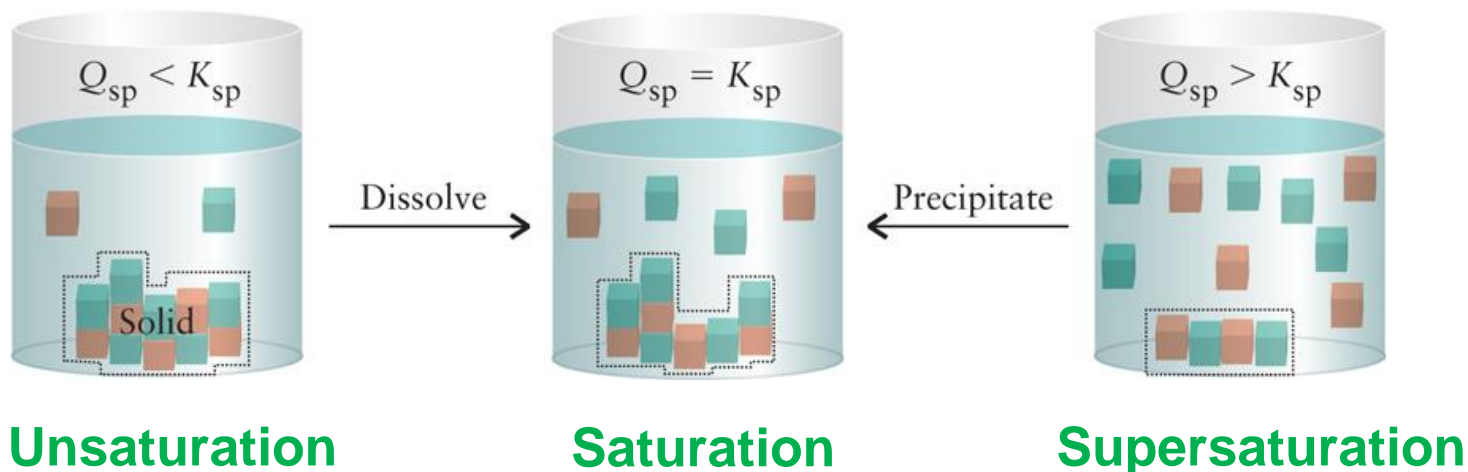


**Unsaturation**          **Saturation**          **Supersaturation**

**Practice 11:** Suppose we mix equal volumes of 0.2 M $Pb(NO_3)_2$(aq) and KI(aq). Will lead(II) iodide precipitate? $K_{sp} = 1.4 \times 10^{-8}$

The concentrations of the $Pb^{2+}$ and $I^-$ ions are high, and we can expect that precipitation will be spontaneous.

We will calculate a $Q_{sp}$, and if $Q_{sp} > K_{sp}$ we know it will precipitate.

Here a few drops of KI precipitates out the $Pb^{2+}$ as $PbI_2$.

**Practice 11:** Suppose we mix equal volumes of 0.2 M $Pb(NO_3)_2$(aq) and KI(aq). Will lead(II) iodide precipitate? $K_{sp} = 1.4 \times 10^{-8}$

Adding two solutions together means our volumes are changing, which means the concentrations are changing. Assuming we have 1 liter of each solution, with a total volume of 2 liters, we can use our dilution formula $M_1V_1 = M_2V_2$.

$$[Pb^{+2}] = \frac{0.2 \text{ M} \times 1 \text{ L}}{2 \text{ L}} = 0.1 \text{ mol·L}^{-1} \qquad [I^-] = \frac{0.2 \text{ M} \times 1 \text{ L}}{2 \text{ L}} = 0.1 \text{ mol·L}^{-1}$$

$Q_{sp} = [Pb^{+2}][I^-]^2 = (0.1)(0.1)^2 = 1.0 \times 10^{-3} >>> K_{sp}$ so it will precipitate.