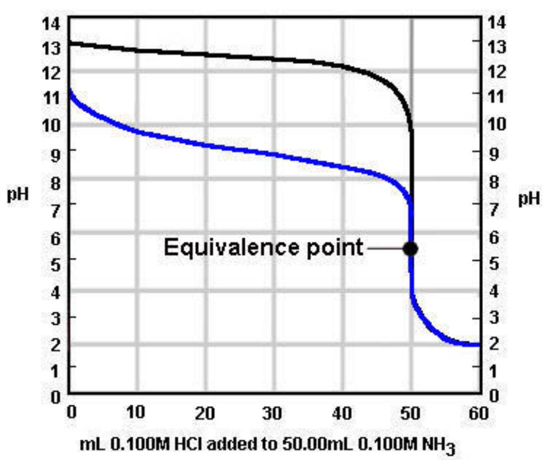
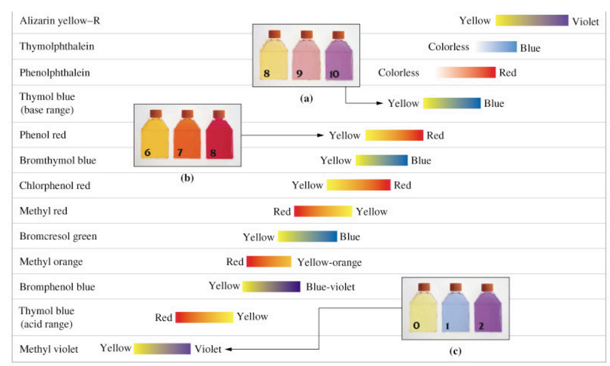
Chapter 17:
Ionic Equilibria in Aqueous Systems





$$pH = pK_a + \log [A^-]/[HA]$$

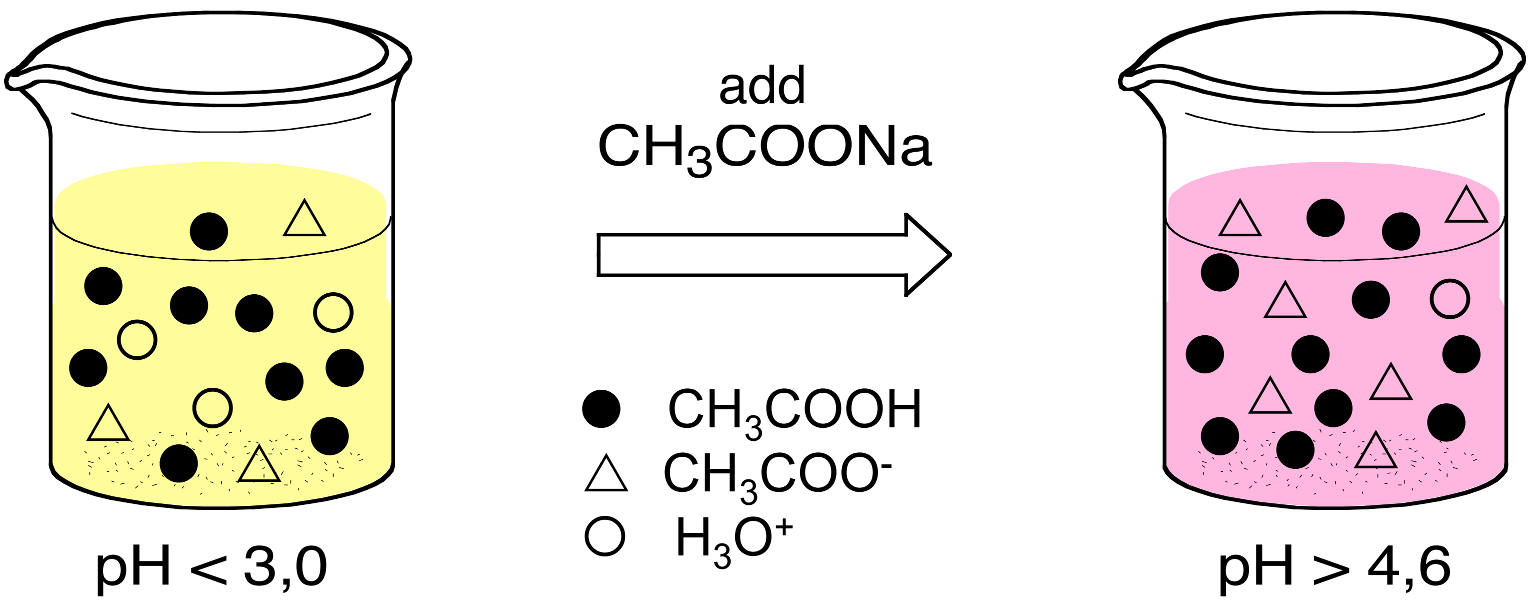
The Common-Ion Effect

- addition of an common ion to an acid-base equilibrium will cause it to shift in order to counter-act that addition
- consequence: limitation on the dissociation of weak acids and bases!

$$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$$

If we add a salt of the conjugate base (e.g. NaA), according to Le Chatelier's Principle, the equilibrium will move to the left)

	$CH_3COOH(aq)$ +	$H_2O(l)$ ⇆	$H_3O^+(aq)$ +	$CH_3COO^-(aq)$
Initial	12	–		
Change		–		
Equilibrium		–		
Add		–		+5
Initial		–		
Change		–		
Equilibrium		–		



Some real numbers…

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

TABLE 17.1 The Effect of Added Acetate Ion on the Dissociation of Acetic Acid

$[CH_3COOH]_{init}$	$[CH_3COO^-]_{added}$	% Dissociation*	H_3O^+	pH
0.10	0.00	1.3	1.3×10^{-3}	2.89
0.10	0.050	0.036	3.6×10^{-5}	4.44
0.10	0.10	0.018	1.8×10^{-5}	4.74
0.10	0.15	0.012	1.2×10^{-5}	4.92

$$*\% \text{ Dissociation} = \frac{[CH_3COOH]_{dissoc}}{[CH_3COOH]_{init}} \times 100$$

Your Turn…

What is the effect on the pH of adding NH_4Cl to a solution of 0.25 M $NH_3(aq)$?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

A. the pH will increase

B. the pH will decrease

C. the pH will not change

D. I'm not sure

Example: Common Ion Effect and pH

What is the quantitative effect on the pH of adding 0.10 *M* NH_4Cl to 0.25 *M* $NH_3(aq)$?

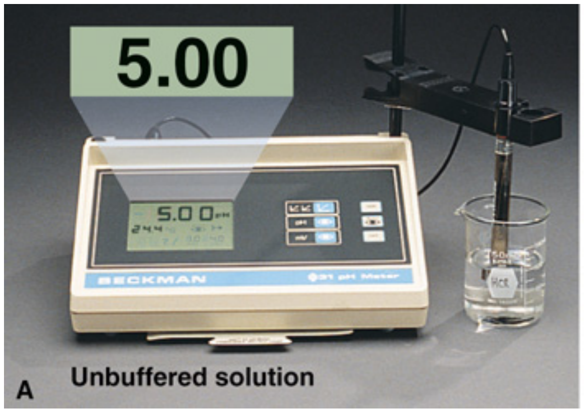
$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

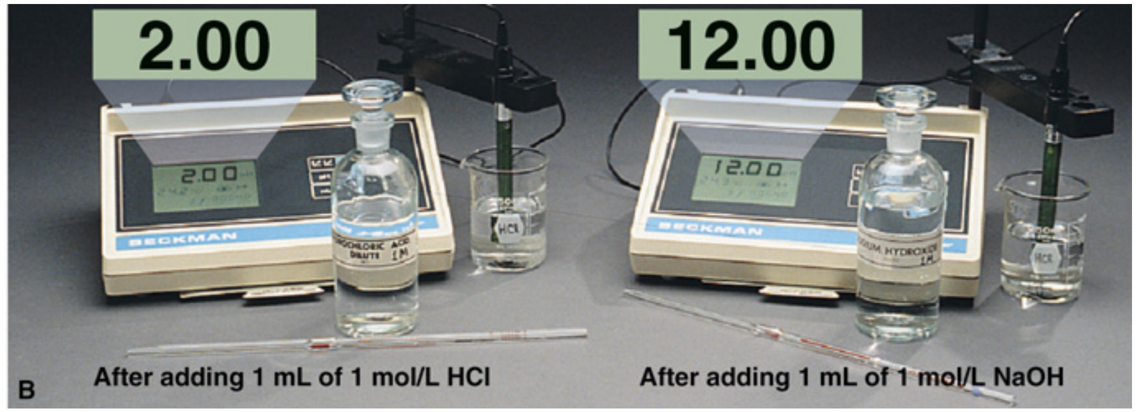
Buffer Solutions

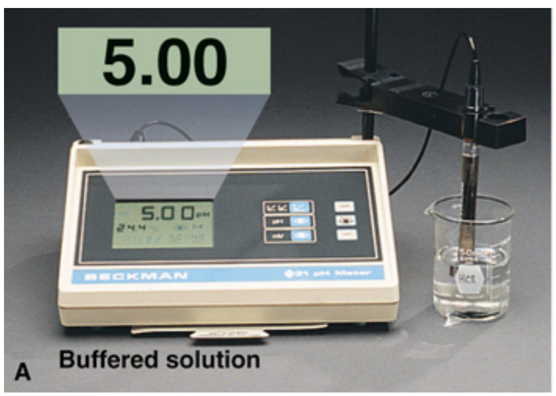
- The function of a buffer is to resist changes in the pH of a solution when either H_3O^+ or OH^- are added
- Buffers are just a special case of the common ion effect

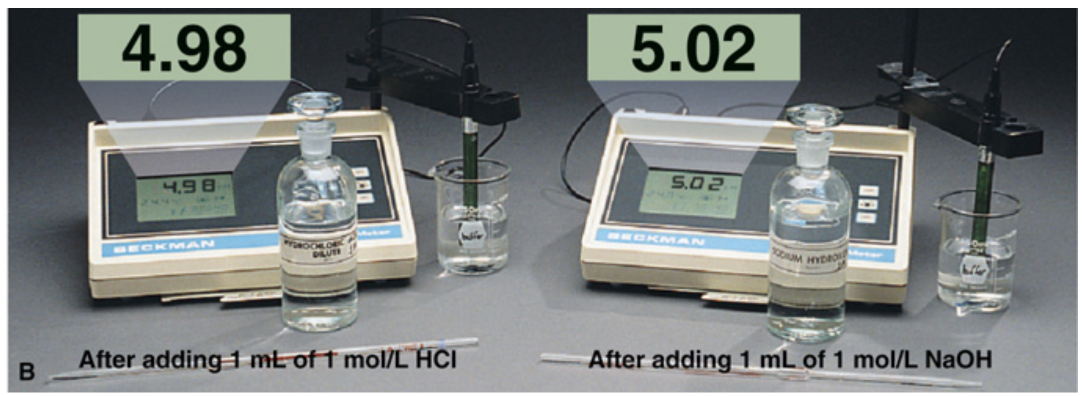
a weak acid or base **+** the corresponding salt of that acid or base

Buffer Solutions









Buffered Solution Characteristics

- in a buffer solution, the acid and base must not neutralize one another
  - we must therefore use ______________________
- a buffer contains relatively high amounts of a weak acid and its conjugate base (or vice-versa)
  - if H_3O^+ is added, it will react with the _________
  - if OH^- is added, it will react with the _________
- the pH is determined by the _________ of the concentrations of the acid and base

Preparing a Buffer Solution

- Preparing a buffer: acid + salt of the conjugate base

+ =

Buffer Solutions

Consider the case where $[CH_3COOH] = [CH_3COO^-]$ in a solution.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8x10^{-5}$$

$$[H_3O^+] = K_a \frac{[CH_3COO^-]}{[CH_3COOH]} = 1.8x10^{-5}$$

$$pH = -log[H_3O^+] = -logK_a = -log(1.8x10^{-5}) = 4.74$$

Example: Preparing a buffer solution

What is the pH of a buffer that has $[CH_3COOH]$ = 0.700 M and $[CH_3COO^-]$ = 0.600 M?

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

pH of Buffer Solutions

Note that whenever we use the assumption we get:

$$K_a = \frac{[H_3O^+]([A^-]_o + x)}{([HA]_o - x)} = \frac{[H_3O^+][A^-]_o}{[HA]_o}$$

$$\therefore [H_3O^+] = \frac{[HA]_o}{[A^-]_o} \bullet K_a$$

...so this gives us a general equation to find the pH (or for finding the [HA]/[A^-] ratio) in a buffer solution!

Your Turn…

Without using a calculator, which of the following HA/A^- buffers has the lowest pH?

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = 4.8 \times 10^{-5}$$

A. 0.100 M HA / 0.200 M A^-

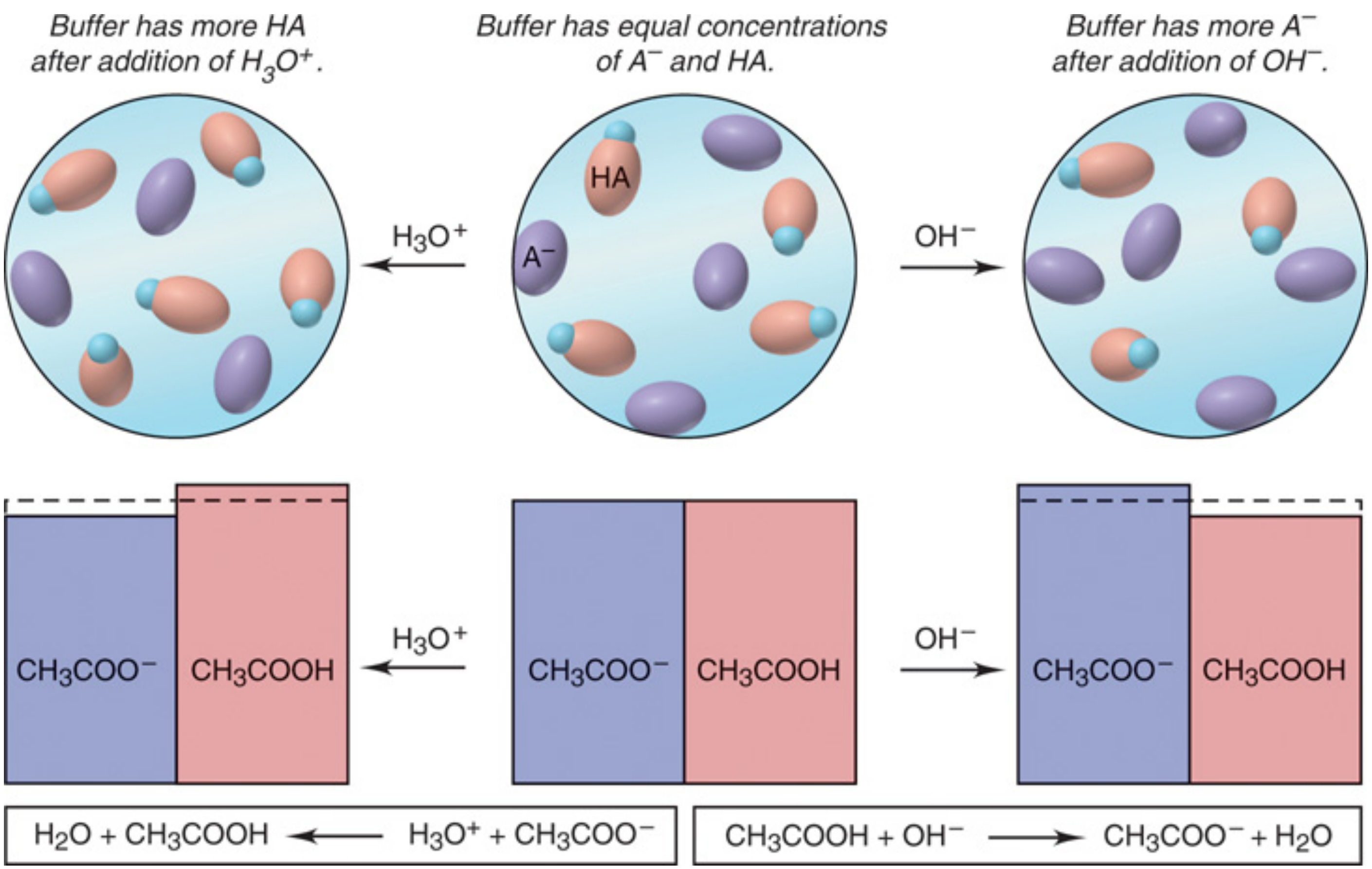
B. 0.200 M HA / 0.200 M A^-

C. 0.200 M HA / 0.100 M A^-

D. I'm not sure

Why Does Buffering Work?

$$[H_3O^+] \propto \frac{[HA]_o}{[A^-]_o}$$



Example: Playing with buffers

To a 100 mL buffer solution of 0.500 M CH_3COOH/ 0.500 M CH_3COONa, 1.00x10^{-3} mol of NaOH was added. What is the change in pH?

This is a two-step problem:

1. stoichiometry of acid-base reaction:

   Work out the neutralization of the added acid or base

2. equilibrium calculation

   Calculate the new equilibrium for your weak acid or base

Example, Part 2: *without buffering*

To a 100 mL solution of 0.500 M CH_3COOH, $1.00x10^{-3}$ mol of NaOH was added. What is the change in pH?

Key Points on Buffered Solutions

1. They are weak acids or bases containing a common ion.

2. After addition of strong acid or base, deal with neutralization first, then equilibrium.

The Henderson-Hasselbalch Equation

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \therefore [H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

$$-\log[H_3O^+] = -\log\left(\frac{K_a[HA]}{[A^-]}\right)$$

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

The Henderson-Hasselbalch Equation

… useful for calculating pH when the [A-]/[HA] ratios are known!

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Your Turn…

According to the H-H equation, when [HA] = [A^-], the pH is equal to:

A. 1

B. 0

C. -pK_a

D. pK_a

The Henderson-Hasselbalch Equation

- note that a buffer solution is most effective when ______________, or:

$$\log \frac{[A^-]}{[HA]} \approx \log(1.0) \approx 0.0$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \approx pK_a$$

- therefore, a buffer solution is most effective when:

____

The Henderson-Hasselbalch Equation

- 2 key criteria for buffer solutions:

1.
$$0.1 < \frac{[A^-]}{[HA]} < 10$$

2.
$$[A^-] > 100 \times K_a$$

and

$$[HA] > 100 \times K_a$$

Example: Using the HH equation

25.0 g of propionic acid (CH_3CH_2COOH) and 36.2 g of sodium propionate (CH_3CH_2COONa) are mixed in a 1.00 L of solution. What is the pH?

$K_a = 1.30 \times 10^{-5}$

Six Methods of Preparing Buffer Solutions

Weak acid (HA)

Titrate with NaOH

$$HA + OH^- \longrightarrow A^- + H_2O$$

to adjust

$$\frac{[HA]}{[A^-]}$$

to give

Weak base (B)

Titrate with HCl

$$B + H^+ \longrightarrow BH^+$$

to adjust

$$\frac{[BH^+]}{[B]}$$

to give

Weak acid (HA) and salt (NaA)

Mix HA and A^- to give

Desired pH

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

$$[H_3O^+] = K_a \frac{[BH^+]}{[B]}$$

$$= \frac{K_w}{K_b} \frac{[BH^+]}{[B]}$$

Weak base (B) and salt (BHCl)

Mix B and BH^+ to give

Salt of weak acid (NaA)

Titrate with HCl

$$A^- + H^+ \longrightarrow HA$$

to adjust

$$\frac{[HA]}{[A^-]}$$

to give

Salt of weak base (BHCl)

Titrate with NaOH

$$BH^+ + OH^- \longrightarrow B + H_2O$$

to adjust

$$\frac{[BH^+]}{[B]}$$

to give

Example: Preparing a buffer

How would you prepare a so-called "carbonate buffer" solution with a pH of 10.10? You are supplied with H_2CO_3, $NaHCO_3$, and Na_2CO_3.

K_a of $H_2CO_3 = 4.2 \times 10^{-7}$ $\therefore$ $pK_a = 6.38$

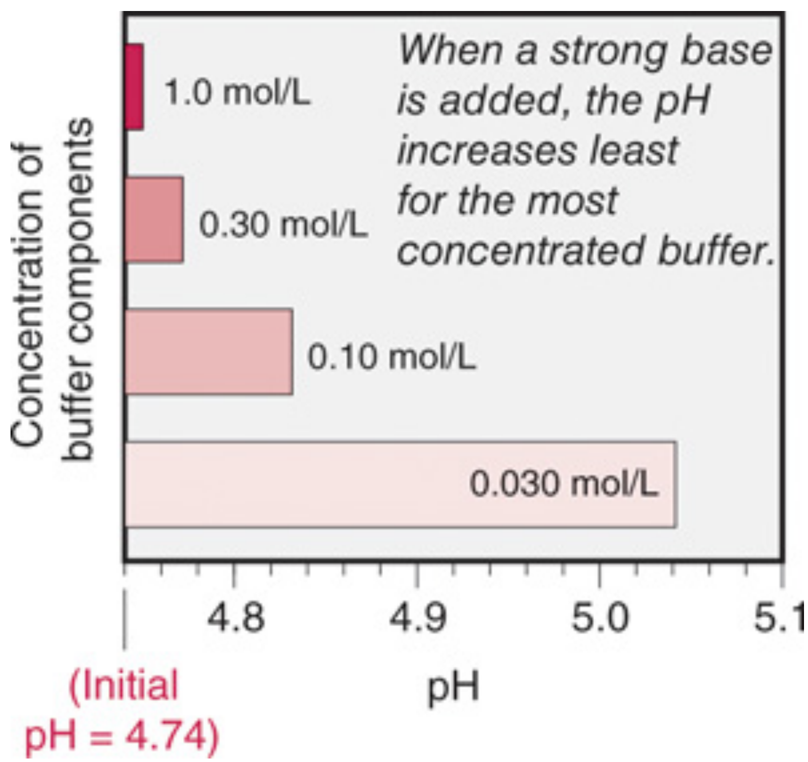
K_a of $HCO_3^- = 4.8 \times 10^{-11}$ $\therefore$ $pK_a = 10.32$

Buffer Capacity and Range

- **Buffer capacity** is the amount of acid or base that a buffer can neutralize before its pH changes appreciably.
  - Maximum buffer capacity exists when [HA] and [A-] are large and approximately equal to each other.
- **Buffer range** is the pH range over which a buffer effectively neutralizes added acids and bases.
  - Practically, range is 2 pH units around pK_a
  - or: ____________

Buffer Capacity Illustrated

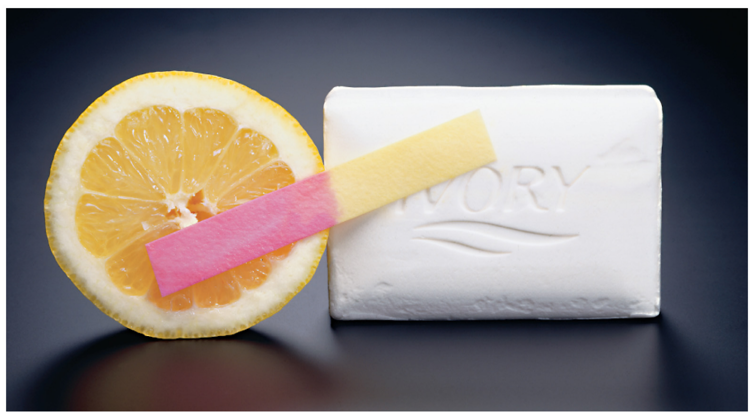
4 different CH_3COOH/CH_3COO^- buffers:



Acid-Base Reactions

- acid-base reactions are known as neutralizations
- they have the general formula:

- the "driving force" is the formation of water



Acid-Base Reactions

Consider the following acid-base reaction:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H2O(l)$$

- *The molecular equation is:*

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

- *The ionic equation is:*

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

- *The net ionic equation is therefore:*

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

Some terminology…

- **a titration:** a solution of known, precise concentration (the standard solution) is gradually added to a solution of unknown concentration

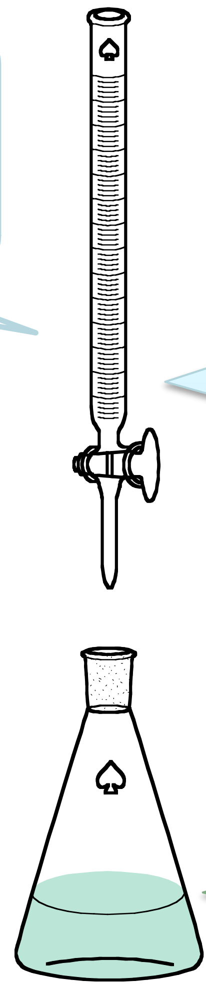
- **the equivalence point:** the point at which the reaction is completed; for an acid-base neutralization this occurs when:

  ____

- **the indicator:** signals the __________________ (close to the equivalence point), usually by changing colour

The Titration Set-up

burette: contains standard solution

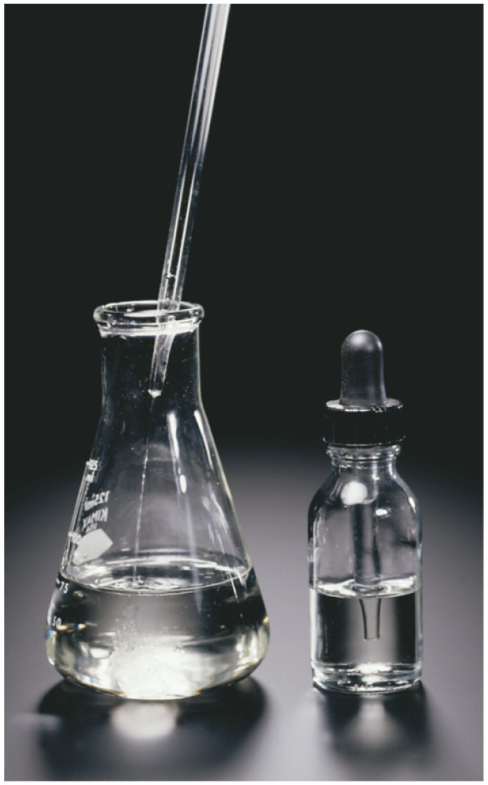


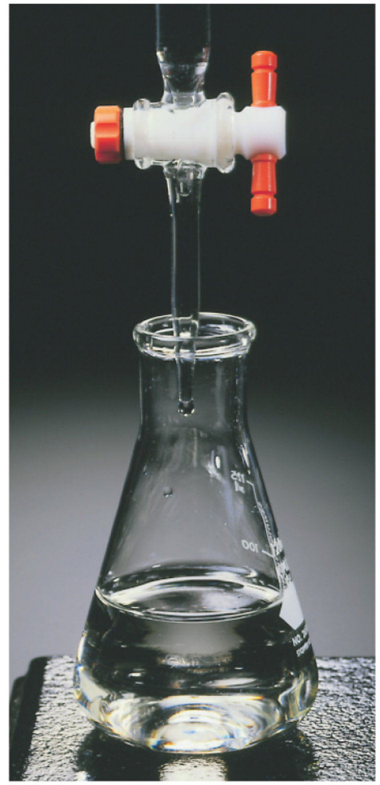
C known
V added known

Erlenmeyer flask:
contains unknown solution

V known
C = ???

The titration procedure…





1) Add precisely known volume of sample (ex. 50.00 mL via pipette)

2) Add a few drops of indicator (ex. phenolphthalein)

3) Carefully add titrant (drop-by-drop, if possible)

4) The endpoint: note the precise volume of titrant added

Your Turn…

25.00 mL of HCl requires 50.00 mL of 0.1 M NaOH for titration to the equivalence point. What is the concentration of the HCl?

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

A. 0.1 M

B. 0.01 M

C. 0.05 M

D. 0.2 M

Example: Titrations and stoichiometry

Apples contain malic acid, $H_2C_4H_4O_5$. 76.80 g of apple requires 34.56 mL of 0.663 M NaOH for titration. What is the mass % of malic acid in these apples?

$$H_2C_4H_4O_5(aq) + 2\ NaOH(aq) \rightarrow Na_2C_4H_4O_5(aq) + 2\ H_2O(l)$$

Acid-Base Indicators

Colour of some substances depends on the pH:

$$\mathbf{HIn} + H_2O \rightleftharpoons \mathbf{In^-} + H_3O^+$$

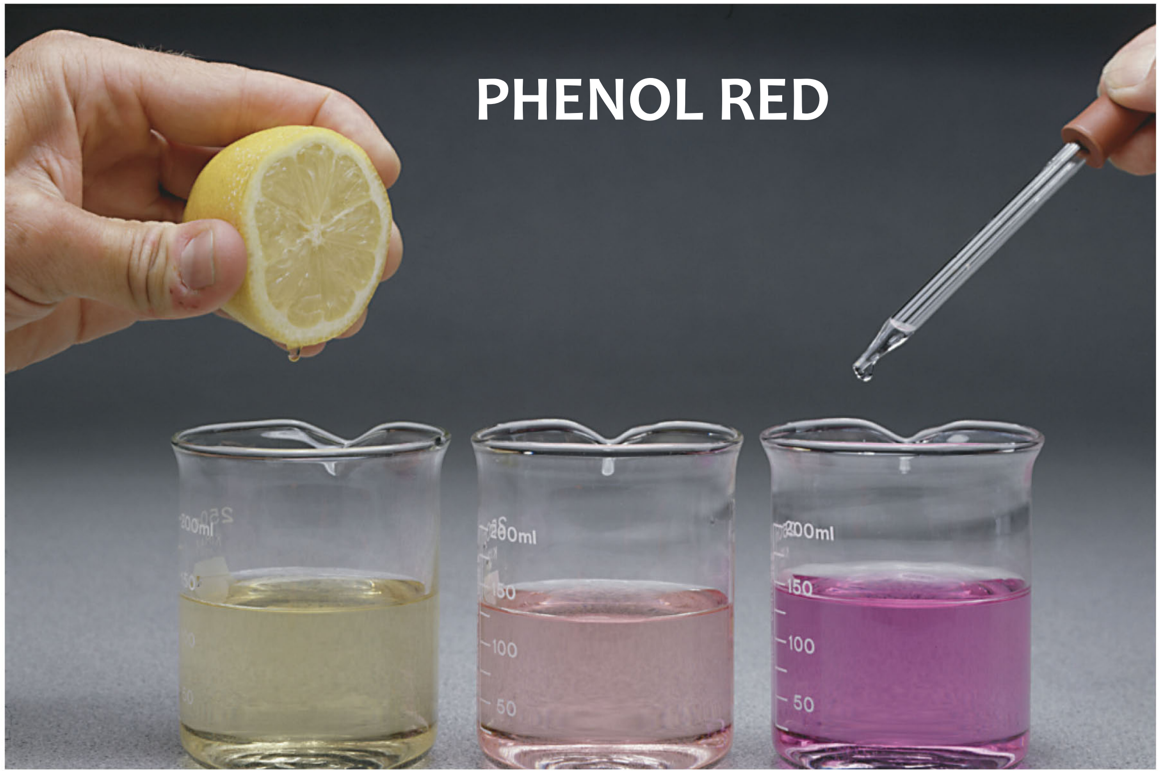
>90% acid form = appears as the acid colour

>90% base form = appears to be the base colour

Intermediate colour is seen in between these two states.

Complete colour change occurs over 2 pH units.

Acid-Base Indicators

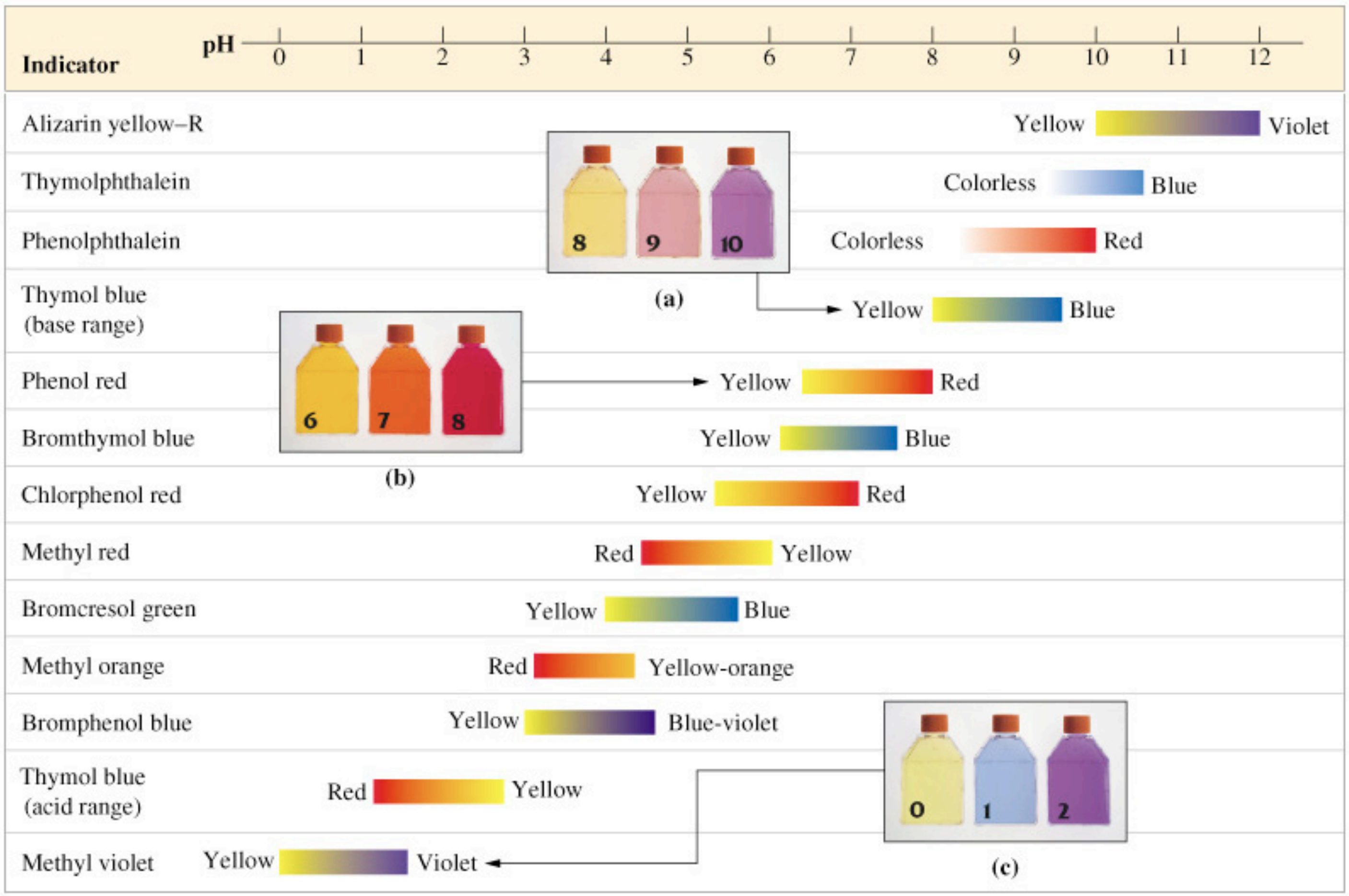


pH < 6.6
YELLOW

6.6 < pH < 8.2
ORANGE

pH > 8.2
PINK

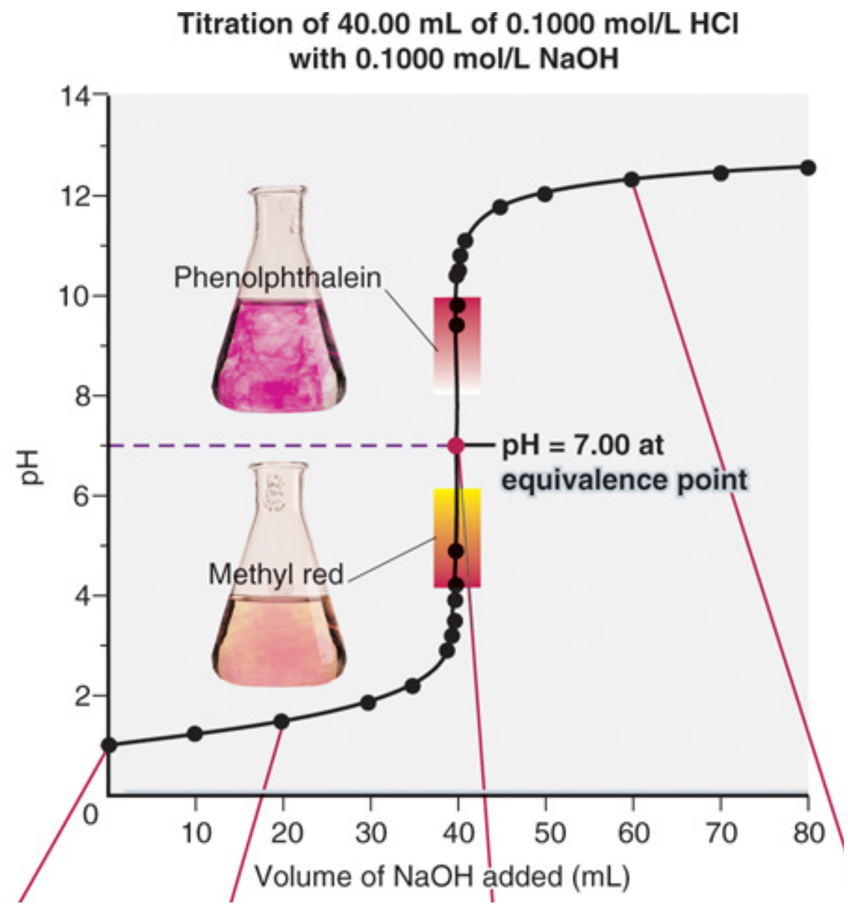
Indicator Colors and Ranges



Titration Curves: Strong Acid + Strong Base

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

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.10
40.05	9.80
40.10	10.10
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52



initial pH: $pH = -\log[H_3O^+]_o$

adding OH^-: OH^- is the LR; use neutr'n table to find excess $[H_3O^+]$ and then pH

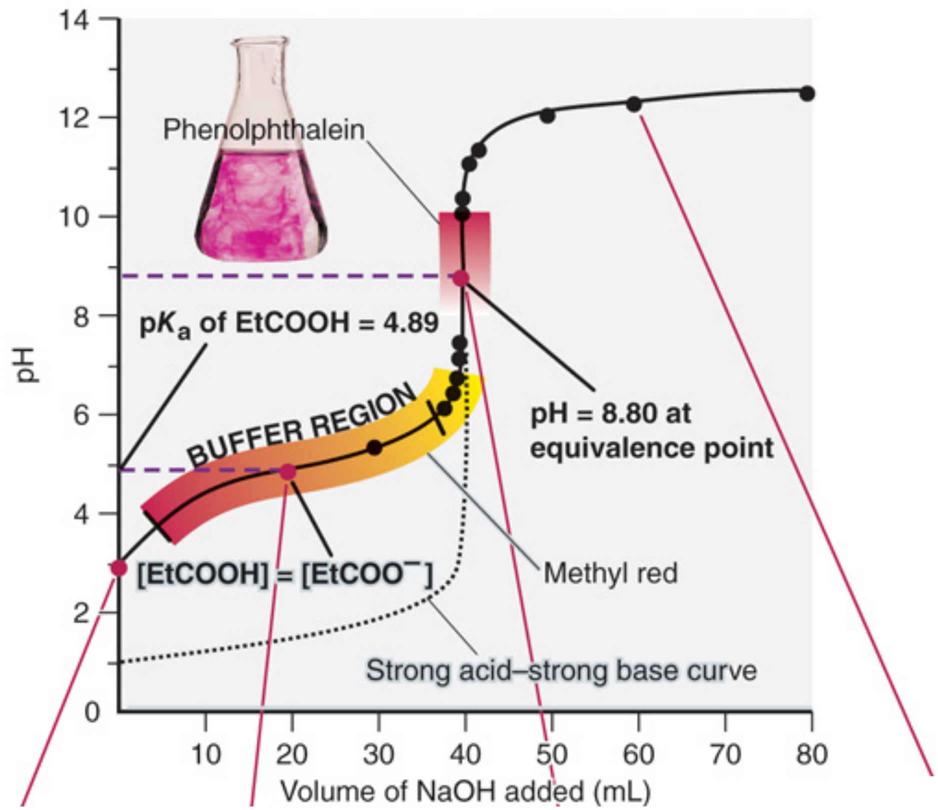
equivalence point: mol H_3O^+ = mol OH^-; thus pH = 7

adding more OH^-: OH^- is now in excess, so find pOH and then pH

Titration Curves: Weak Acid + Strong Base

$$CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_2CH_3COONa(aq) + H_2O(l)$$

Titration of 40.00 mL of 0.1000 mol/L EtCOOH with 0.1000 mol/L NaOH



initial pH: use ICE table to find $[H_3O^+]$, then pH = $-\log[H_3O^+]$

adding OH^-: OH^- is the LR; use neutr'n table to find [HA] and $[A^-]$; use ICE table or HH equation to find pH

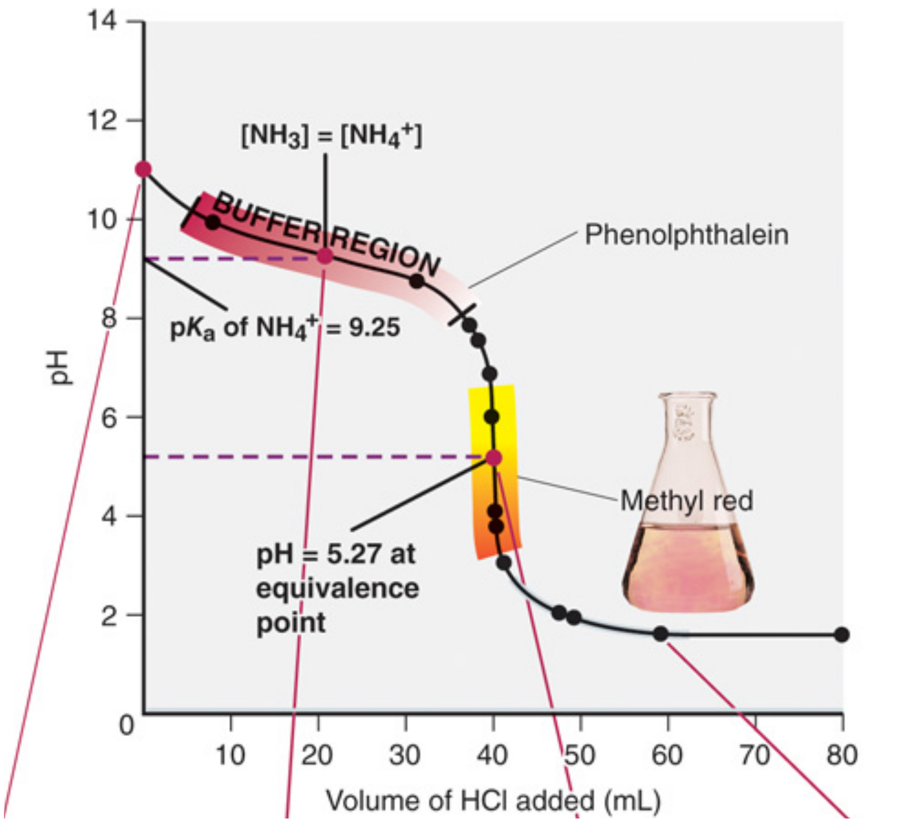
equivalence point: mol HA = mol OH^-; HA is thus converted entirely to A^-; use ICE table and K_b to find $[OH^-]$, then pOH, then pH (note pH > 7)

adding more OH^-: OH^- is now in excess, so find pOH and then pH

Titration Curves: Weak Base+ Strong Acid

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

Titration of 40.00 mL of 0.1000 mol/L NH_3 with 0.1000 mol/L HCl



initial pH: use ICE table to find [OH^-], then pOH and pH

adding H_3O^+: $H_3O^+$is the LR; use neutr'n table to find [B] and [HB^+]; use ICE table or HH equation to find pH

equivalence point: mol B = mol H_3O^+; B is thus converted entirely to HB^+; use ICE table and K_a to find [H_3O^+], then pH (note pH < 7)

adding more H_3O^+: H_3O^+ is now in excess, just find pH

17.3 Slightly Soluble Ionic Compounds

- Equilibrium between a slightly soluble ionic solid and aqueous ions:

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

- When equilibrium has been established, no more AgCl dissolves and the solution is *SATURATED*.

Solubility

What is the SOLUBILITY of AgCl?

Let "s" represent the solubility of AgCl:

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

- When the solution is SATURATED:

  $[Ag^{+}] = 1.67 \times 10^{-5}$ M (by experiment)

- What is [Cl-]?

What is K_{eq}?

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

- Saturated solution has

$$[Ag^+] = [Cl^-] = 1.67 \times 10^{-5}\ M$$

- Using these values to calculate K_{eq}:

$$K_{eq} = [Ag^+][Cl^-]$$

$$= (1.67 \times 10^{-5})(1.67 \times 10^{-5})$$

$$= 2.79 \times 10^{-10}$$

K_{sp}: solubility product constant

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

$$K_{eq} = [Ag^{+}]\,[Cl^{-}] = 2.79 \times 10^{-10} \text{ at } 25°C$$

- Because this is the product of "solubilities", we call it:

$$K_{sp} = \text{solubility product constant}$$

Your Turn…

Which is the correct equilibrium constant expression for the dissolution of Na_2CO_3 (s) ?

A. $[Na^+][CO_3^{2-}]$

B. $[Na^+][CO_3^{2-}]^2$

C. $[Na^+]^2[CO_3^{2-}]$

D. $[2Na^+]^2[CO_3^{2-}]$

E. $[Na^+]^2[CO_3^{2-}]^2$

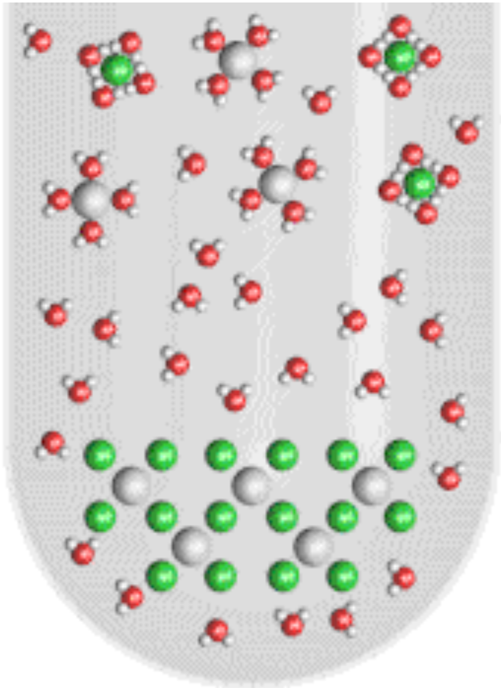
Several Solubility Product Constants at 25°C

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$	1.3×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3{}^{2-}(aq)$	5.1×10^{-9}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$	1.1×10^{-10}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$	2.8×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$	5.3×10^{-9}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4{}^{2-}(aq)$	9.1×10^{-6}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,OH^-(aq)$	6.3×10^{-31}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$	4×10^{-38}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$	1.6×10^{-5}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4{}^{2-}(aq)$	2.8×10^{-13}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$	7.1×10^{-9}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3{}^{2-}(aq)$	3.5×10^{-8}
Magnesium fluoride	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$	3.7×10^{-8}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$	1.8×10^{-11}
Magnesium phosphate	$Mg_3(PO_4)_2(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4{}^{3-}(aq)$	1×10^{-25}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2{}^{2+}(aq) + 2\,Cl^-(aq)$	1.3×10^{-18}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Silver carbonate	$Ag_2CO_3(s) \rightleftharpoons 2\,Ag^+(aq) + CO_3{}^{2-}(aq)$	8.5×10^{-12}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Silver chromate	$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4{}^{2-}(aq)$	1.1×10^{-12}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.5×10^{-17}

Lead(II) Chloride

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

$$K_{sp} = 1.9 \times 10^{-5}$$



Solubility versus Solubility Product Constant

- Note the difference between these two values:
  - solubility = amount of solute per amount of solution

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

solubility = 0.000 246 g per 100 g of water at 25°C!

  - solubility product constant = equilibrium constant

$$PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2\ Cl^{-}(aq)$$

$K_{sp} = [Pb^{2+}][Cl^{-}]^2$

Solubility versus Solubility Product Constant

- K_{sp} can be related to the *solubility*, but sometimes we can't compare the solubilities of two different compounds based solely on K_{sp}:

$$AgCl(s) \leftrightharpoons Ag^{+}(aq) + Cl^{-}(aq) \quad K_{sp} = [Ag^{+}][Cl^{-}]$$

$$PbCl_2(s) \leftrightharpoons Pb^{2+}(aq) + 2\,Cl^{-}(aq) \quad K_{sp} = [Pb^{2+}][Cl^{-}]^2$$

- there are two ways to express solubility:

$$\text{solubility} = \frac{\text{g solute}}{\text{L saturated solution}}$$

$$\text{molar solubility} = \frac{\text{mol solute}}{\text{L saturated solution}}$$

- Note: the solubility of a compound depends on temperature

Solving Solubility Problems

Solubility of compound → Molar solubility of compound → Ion concentrations → K_{sp} of compound

K_{sp} of compound → Ion concentrations → Molar solubility of compound → Solubility of compound

Example 1: Solubility of Lead Iodide

Consider PbI_2 dissolving in water: $PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^{-}(aq)$

Calculate K_{sp} if its molar solubility is 0.00130 mol/L.

Example 2: Solubility of Silver Chromate

Ag_2CrO_4 dissolves in water: $Ag_2CrO_4(s) \rightleftarrows 2Ag^{+}(aq) + CrO_4^{2-}(aq)$

Calculate its molar solubility if its K_{sp} is 1.1×10^{-12}.

The Common Ion Effect

$$PbCrO_4\,(s) \rightleftarrows Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

What happens when Na_2CrO_4 (s) is added?

$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	$PbCrO_4(s) \leftarrow Pb^{2+}(aq) + CrO_4^{2-}(aq\text{; added})$

Your Turn…

To improve the quality of X-ray photos used in the diagnosis of intestinal disorders the patient drinks an aqueous suspension of $BaSO_4$ before having the X-ray. However, $BaSO_4$ is slightly soluble (K_{sp} = 1.1x10^{-10}) and Ba^{2+} is toxic. Which of the following compounds would be the best to add to the suspension in order to make it less concentrated in Ba^{2+} and less toxic to the patient?

A. $NaNO_3$

B. $Ba(NO_3)_2$

C. NaCl

D. H_2SO_4

E. Na_2SO_4

Example: Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M Na_2SO_4. K_{sp} for $BaSO_4 = 1.1 \times 10^{-10}$

pH and Solubility

- pH can also affect the solubilities of some compounds
- consider the following equilibrium:

$$Co(OH)_2(s) \leftrightarrows Co^{2+}(aq) + 2\ OH^{-}(aq)$$

$$K_{sp} = 2.5 \times 10^{-16} = [Co^{2+}][OH^{-}]^2$$

pH **solubility**

pH **solubility**

Comparing the solubilities…

Pure water: $[OH^-] = 1 \times 10^{-7}$ M

	$Co(OH)_2(s)$ ⇄	$Co^{2+}(aq)$	+ 2 $OH^-(aq)$
I	–	0	$1x10^{-7}$
C	–	+s	+2s
E	–	s	$1x10^{-7}$ + 2s

$$K_{sp} = (s)(1.0x10^{-7} + 2s)^2$$

$$K_{sp} \approx (s)(2s)^2$$

$$s = 4.0x10^{-6} \text{ M}$$

pH = 6 buffer: $[OH^-] = 1 \times 10^{-8}$M

	$Co(OH)_2(s)$ ⇄	$Co^{2+}(aq)$	+ 2 $OH^-(aq)$
I	–	0	$1x10^{-8}$
C	–	+s	no change!
E	–	s	$1x10^{-8}$

$$K_{sp} = (s)(1.0x10^{-8})^2$$

$$s = \frac{K_{sp}}{(1.0x10^{-8})^2}$$

$$s = 2.5 \text{ M}$$

Why so soluble in acid?

$Co(OH)_2\,(s) \leftrightarrows Co^{2+}(aq) + 2\,OH^-(aq)$ $\qquad K_{sp} = 2.5\text{x}\,10^{-16}$

$OH^-(aq) + H_3O^+(aq) \leftrightarrows 2\,H_2O(l)$ $\qquad K = 1/K_w = 1.0\text{x}10^{14}$

$2\,OH^-(aq) + 2\,H_3O^+(aq) \leftrightarrows 4\,H_2O(l)$ $\qquad K' = (1/K_w)^2 = 1.0\text{x}10^{28}$

$Co(OH)_2\,(s) + 2H_3O^+(aq) \leftrightarrows Co^{2+}(aq) + 4\,H_2O(l)$

$$K = K_{sp}(1/K_w)^2 = (2.5\text{x}10^{-16})(1.0\text{x}10^{28}) = 2.5\text{x}10^{12}$$

Your Turn…

How many of the following compounds would be less soluble in a pH = 10.00 buffer than in pure water?

$PbCl_2$ $Ba(OH)_2$ Hg_2I_2 CaF_2

A. None of them.

B. 1

C. 2

D. 3

E. All of them.

Ksp and Precipitation

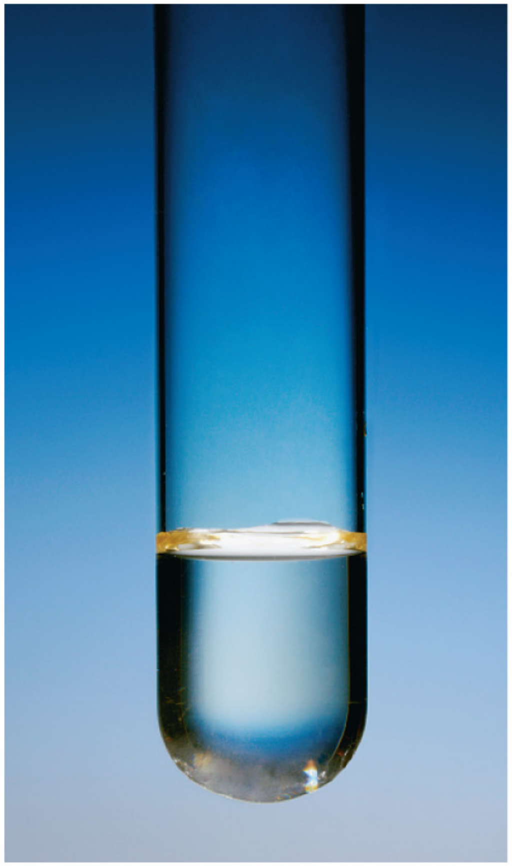
- K_{sp} = the product of the maximum ion concentrations allowed in a saturated solution
- precipitation begins when the product surpasses K_{sp}, or:

$$Q > K_{sp}$$

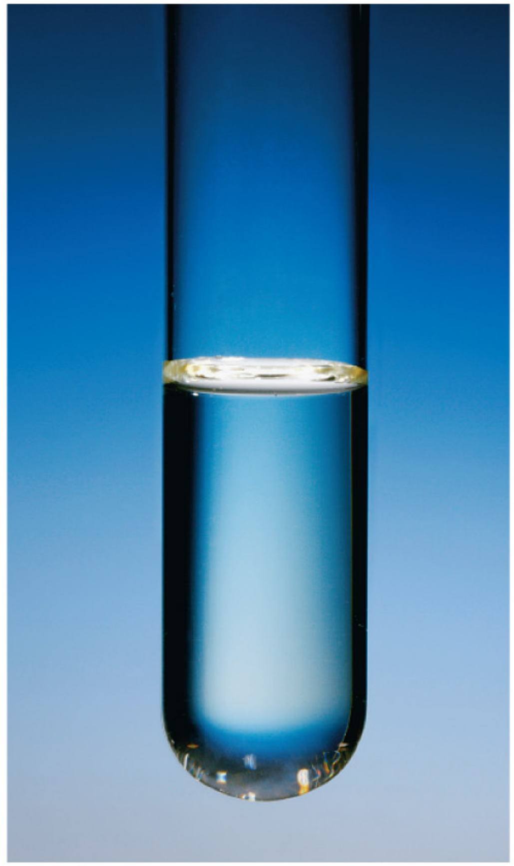
The Solubility Product and Q

- Q again has the same formula as K_{sp}, but the values used are the initial concentrations, not necessarily those at equilibrium
- if $Q < K_{sp}$, the solution is ________________ (i.e., more solid can be dissolved until $Q = K_{sp}$)
- if $Q = K_{sp}$, the solution is ________________ (i.e., the system is at equilibrium)
- if $Q > K_{sp}$, the solution is ________________ (i.e., there will be precipitation of solid until $Q = K_{sp}$)

An example: $AgNO_3$ + NaI



$AgNO_3(aq)$



NaI(aq)

AgI(s)

$Na^+(aq)$ $NO_3^-(aq)$

Precipitation Reactions

- how can we predict when a precipitate will form?

> By knowing the solubilities
> of inorganic compounds

- two categories:
  - soluble
  - sparingly (or slightly) soluble

Solubility Rules (p 721)

TABLE 17.4 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds	Insoluble Ionic Compounds
1. All common compounds of Group 1 ions (such as Li^+, Na^+, and K^+) and the ammonium ion (NH_4^+) are soluble.	1. All common metal hydroxides are insoluble, *except* those of Group 1 ions and the larger members of Group 2 (beginning with Ca^{2+}).
2. All common nitrates (NO_3^-), acetates (CH_3COO^- and $C_2H_3O_2^-$), and most perchlorates (ClO_4^-) are soluble.	2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, except those of Group 1 ions and NH_4^+.
3. All common chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, except those of Ag^+, Pb^{2+}, Cu^+, and Hg_2^{2+}. All common fluorides (F^-) are soluble, *except* those of Pb^{2+} and Group 2 ions.	3. All common sulfides are insoluble, except those of Group 1 ions, Group 2 ions, and NH_4^+.
4. All common sulfates (SO_4^{2-}) are soluble, except those of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, and Pb^{2+}.	

Predicting Precipitation Reactions

Predict the outcome (if any) when the following solutions are mixed together. Give a balanced net ionic equation.

$NaBr(aq) + Pb(NO_3)_2\ (aq)$

$Fe(NO_3)_3(aq)\ + NaOH(aq)$

$HI(aq)\ +\ ZnCl_2(aq)$

Example 1: Precipitating an insoluble salt

$Hg_2Cl_2(s) \rightleftarrows Hg_2^{2+}(aq) + 2\ Cl^-(aq)$ $K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$

If $[Hg_2^{2+}] = 0.010$ M, what $[Cl^-]$ is required to just begin the precipitation of Hg_2Cl_2?

In other words, this problem is asking: what is the maximum $[Cl^-]$ that can be in solution with 0.010 M Hg_2^{2+} *before* Hg_2Cl_2 (s) begins to form?

Example 2: Precipitating an insoluble salt

$Hg_2Cl_2(s) \rightleftarrows Hg_2^{2+}(aq) + 2\ Cl^-(aq)$ $K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$

Now let's raise $[Cl^-]$ to 1.0 M. What is the value of $[Hg_2^{2+}]$ at this point?

Example 3: Selective Precipitation of Ions

A solution contains 0.020 M Ag^+ and Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. Which precipitates first? How much of the first cation remains in solution when the second cation begins to precipitate?

K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12}$ K_{sp} for $PbCrO_4 = 1.8 \times 10^{-14}$

The substance whose K_{sp} is *first exceeded* precipitates first.

The ion requiring the *lesser amount* of CrO_4^{2-} precipitates first.

Example: Integrative Question

2006 Final Exam

Find the maximum mass of $MgCl_2$ that can be added to 1.00 L of a solution buffered at pH = 10.64 *without* causing precipitation of $Mg(OH)_2$ to occur (assume no volume changes).

$AgNO_3$ is added slowly to the solution above until a precipitate is observed. What is this precipitate? Determine the mass of $AgNO_3$ added at the moment of precipitation.

Chapter 17: Key Concepts

1. Common Ion Effect
2. Buffer solutions
3. The Henderson-Hasselbalch Equation
4. Acid-Base Titrations
5. Solubility product constant, K_{sp}
6. Solubility and K_{sp}
7. Solubility and common ions and pH
8. Precipitation (Q and K_{sp})

Chapter 17: Suggested Problems

17.4, 17.8, 17.9, 17.11, 17.19, 17.21, 17.23, 17.29, 17.31, 17.40, 17.44, 17.52, 17.56, 17.58, 17.61, 17.66, 17.69, 17.72, 17.74, 17.75, 17.79, 17.83, 17.87, 17.91, 17.95, 17.100, 17.114, 17.116, 17.119, 17.122, 17.136, 17.143, 17.147, 17.156, 17.157

- Pay close attention to the titration curve examples on pages 706 to 712