

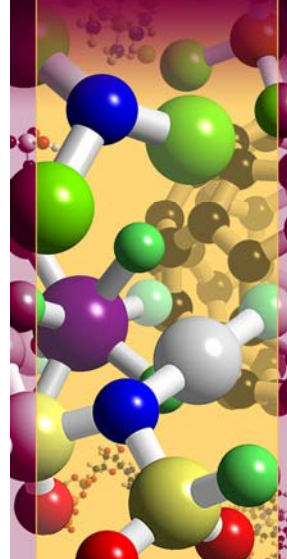
CHEM 1AA3: Intro. Chemistry II

McMaster
University

Chemistry

Acid-Base Chemistry

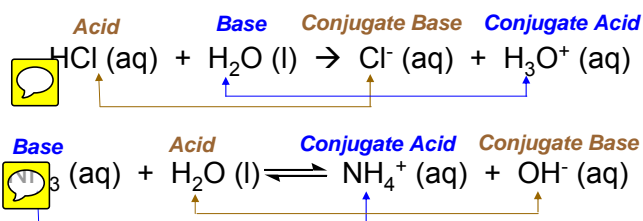
Ch. 17: Additional Aspects of
Acid-Base Equilibria



Acid-Base Chemistry: Review (Ch 16)

Brønsted-Lowry Theory

- **acid** = H⁺ donor, **base** = H⁺ acceptor
- **acid/base** reactants & **conjugate acid/base** products:



- H₂O is an **amphoteric** species (behaves as both an acid or a base)

Refer to Ch. 16-2

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Review: Strong Acids/Bases vs. Weak

- **Strong acids to know (6):**

HCl, HBr, HI, HClO₄, HNO₃, H₂SO₄

- **Strong bases to know:**

Grp I & Grp II hydroxides (many Grp II partially soluble),
hydrides (H⁻) & oxides (O²⁻)



Refer to Ch 16-4


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Review: Strong Acids/Bases vs. Weak

Concept Check:

a) What is the difference between a strong acid (or base) and a weak acid (or base)? 

b) Give an example of: a weak acid, a weak base. 

c) How do you identify whether an acid or base is weak? 

Refer to Ch 16-4

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Review: Strong Acids/Bases vs. Weak

Concept check:

a)

b)

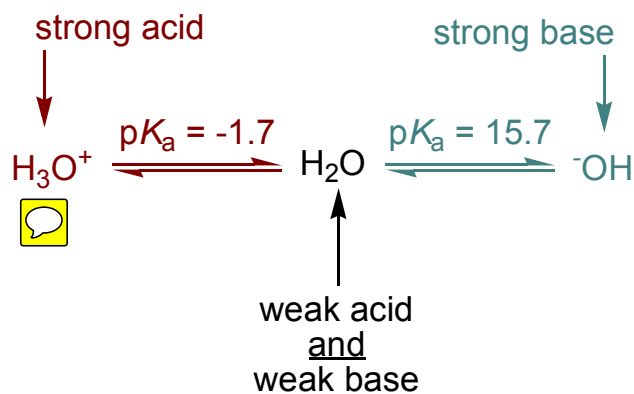
Refer to Ch 16-5

Review: Strong Acids/Bases vs. Weak

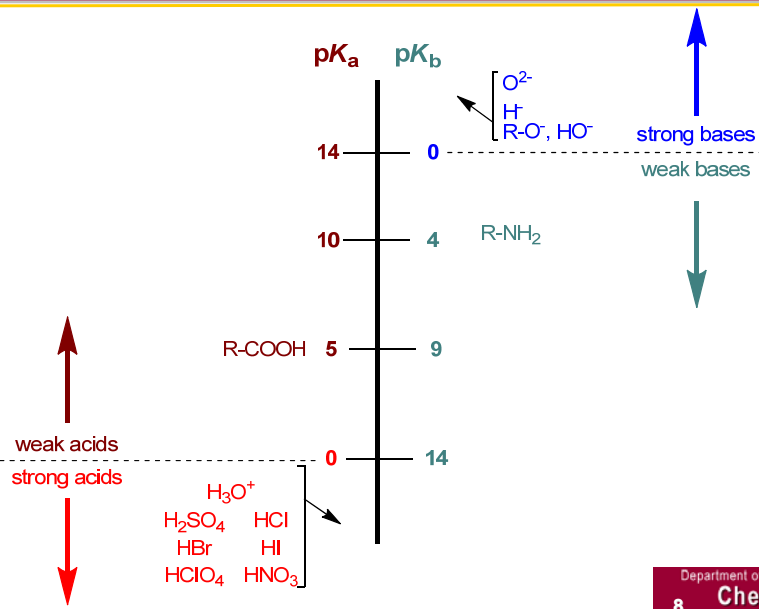
Concept check:

c) 

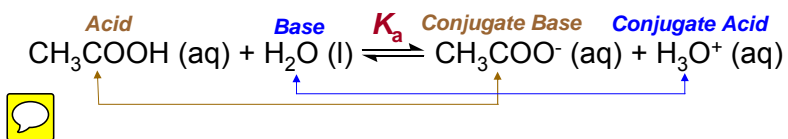
Review: Water is Amphoteric



Review: Typical pK_a Values



Review: Acid-Base Equilibrium: Weak acid & K_a



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

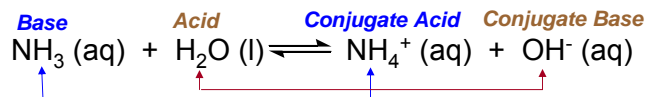
Equilibrium favours reverse process:

Acidity of $\text{H}_3\text{O}^+ > \text{CH}_3\text{COOH}$

Basicity of $\text{CH}_3\text{COO}^- > \text{H}_2\text{O}$

Refer to Ch 16-5

Review: Acid-Base Equilibrium: Weak base & K_b



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

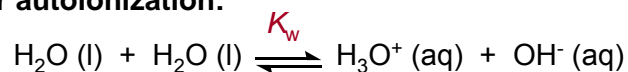
Equilibrium favours reverse process:

Basicity of $\text{OH}^- > \text{NH}_3$

Acidity of $\text{NH}_4^+ > \text{H}_2\text{O}$

Review of relationships we know: pH and pK_w

Water autoionization:



$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \quad (25^\circ\text{C})$$

$$\boxed{\text{p}K_w = \text{pH} + \text{pOH} = 14.0} \quad \text{Aqueous solution}$$

For a conjugate acid-base pair:

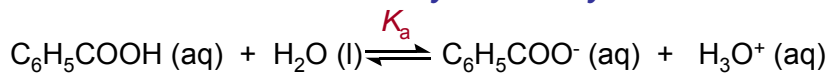
$$\boxed{\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.0}$$

For help with these concepts, see the acid-base podcasts in Avenue, and in Petrucci refer to Ch 16-3 and 16-7

Review: Weak Acids/Bases: Assumptions

Determine the pH and % ionization of a 0.100 M solution of benzoic acid (C₆H₅COOH): K_a = 6.3 × 10⁻⁵

→ Write down the chemistry – correctly!



| | | | | |
|---------|-------------|---|-------|-------|
| Initial | 0.100 M | - | 0 M | 0 M |
| Change | x M | | + x M | + x M |
| Eq'm | 0.100 - x M | | x M | x M |

Refer to Ex 16-6

Review: Weak Acids/Bases: Assumptions

Assuming x is small avoids a quadratic solution...
HOWEVER – we must check if the assumption is valid!

Check: If $\frac{[\text{HA}]}{K_a} > 100$ then assumption is valid (< 5% error):



Then:

and:

% Ionization

$$\frac{[\text{A}^-]}{[\text{HA}]_{\text{initial}}} \times 100 =$$



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Diagnostic iClicker question




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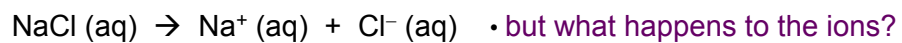


Review: pH of Salt Solutions


Concept Check:

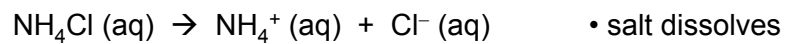
Is the pH of 0.1 M NaCl(aq) acidic, basic, or neutral? 

The salt is soluble, and dissociates in water:



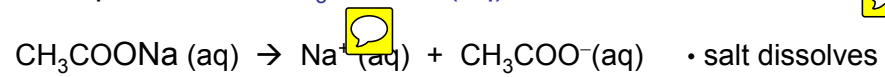
Review: pH of Salt Solutions

Is the pH of 0.1 M NH₄Cl(aq) acidic, basic, or neutral? 



Review: pH of Salt Solutions

Is the pH of 0.1 M CH_3COONa (aq) acidic, basic or neutral? 



Acid-Base Review

- Key concepts





Ch 17: Acid-Base Reactions

- Key to solving acid-base problems is:
 - writing the correct chemistry
 - determining which species acts as a base and which as an acid
 - knowing what remains after the reaction has occurred
- Look for the limiting reagent
 - also look at what remains and what has been formed



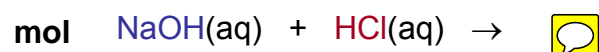
Acid-Base Reactions

- Consider 3 options:
 1. **STRONG BASE** + **STRONG ACID** 
 2. **STRONG BASE** + **weak acid** 
 3. **weak base** + **STRONG ACID**

1. STRONG BASE + STRONG ACID

Limiting reagent: consider moles before & after reaction.

Stoichiometry (mole) table: 

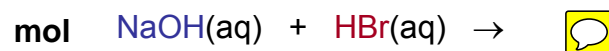


Before   

After   


1. STRONG BASE + STRONG ACID

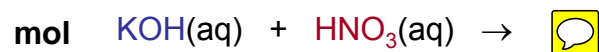


Before 1.3 1.3 -

After   



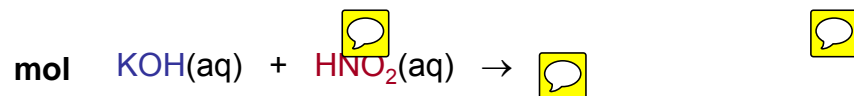
1. STRONG BASE + STRONG ACID



Before 1.2 1.6 -

After

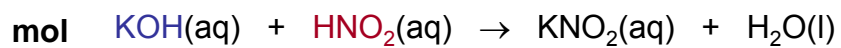
2. STRONG BASE + weak acid









Before 1.3 0.80 -

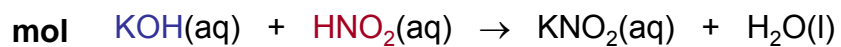
After








2. STRONG BASE + weak acid



| | | | |
|--------|---|---|---|
| Before | 1.1 | 1.1 | - |
| After |  |  |  |
| |  | |  |
| |  | | |

2. STRONG BASE + weak acid



| | | | |
|--------|---|---|---|
| Before | 0.80 | 1.3 | - |
| After |  |  |  |
| |  |  |  |
| |  | | |

3. weak base + STRONG ACID



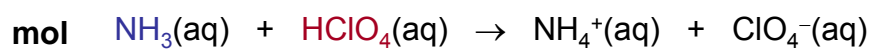
Before 0.60 0.85 -

After   




3. weak base + STRONG ACID



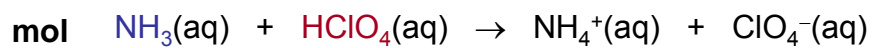
Before 0.75 0.75 -

After    



3. weak base + STRONG ACID



| | | | |
|--------|------|------|---|
| Before | 0.85 | 0.60 | - |
| After | | | |
| | | | |
| | | | |

17.4 Acid-Base Titrations

- Limiting reactant questions: either acid or base is always in excess, except at the **equivalence point***
*(mol acid = mol base for 1:1 acid:base titration)

- In 3 titrations different species are formed as pH changes:

Strong Acid + Strong Base

strong acid → → strong base

Weak Acid + Strong Base

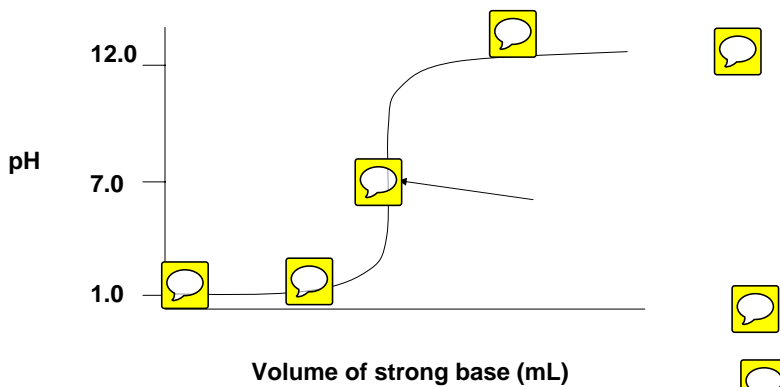
weak acid → **buffer** → → strong base

Weak Base + Strong Acid

weak base → **buffer** → → strong acid

- Not covered: weak acid + weak base.

Strong Acid-Strong Base Titration (Lab 1, 6)



Titrate 25.0 mL 0.100 M HCl(aq) with 0.100 M NaOH(aq)

Practice Calculations: Strong Acid – Strong Base

Titrate 25.0 mL 0.100 M HCl(aq) with 0.100 M NaOH(aq)

- Calculate pH at 4 points:
 - 0 mL NaOH
 - 12.5 mL NaOH
 - 25.0 mL NaOH
 - 37.5 mL NaOH

0 mL NaOH = only strong acid present

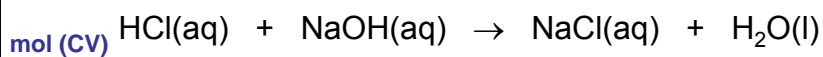
- HCl is a strong acid, so $[\text{H}_3\text{O}^+] = [\text{HCl}]$

pH =

Practice Calculations: Strong Acid – Strong Base

12.5 mL NaOH = ½-equivalence point

- ½ of HCl consumed.




Before




After



- NaCl does not affect pH. 



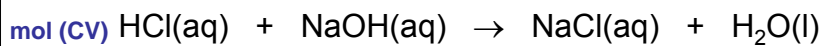
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Practice Calculations: Strong Acid – Strong Base

25.0 mL NaOH = equivalence point

- All HCl consumed.



Before




After



- NaCl does not affect pH.



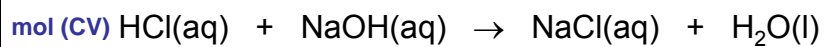
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Practice Calculations: Strong Acid – Strong Base

37.5 mL NaOH = only strong base present

- All HCl consumed; excess NaOH.



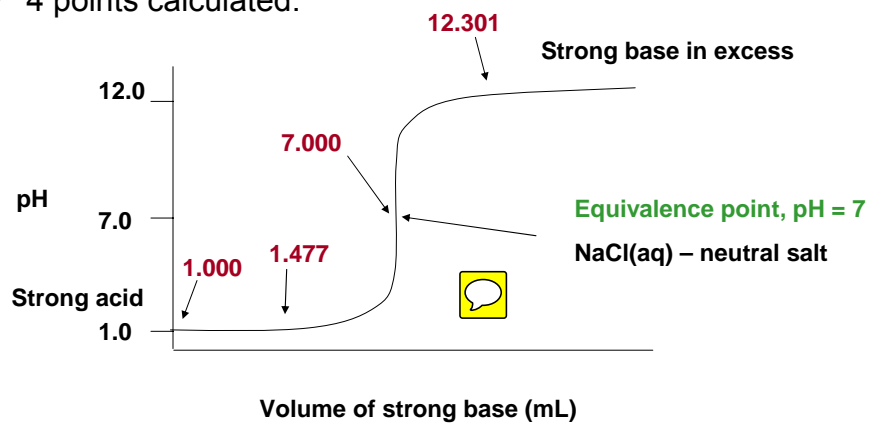
Before   

After   

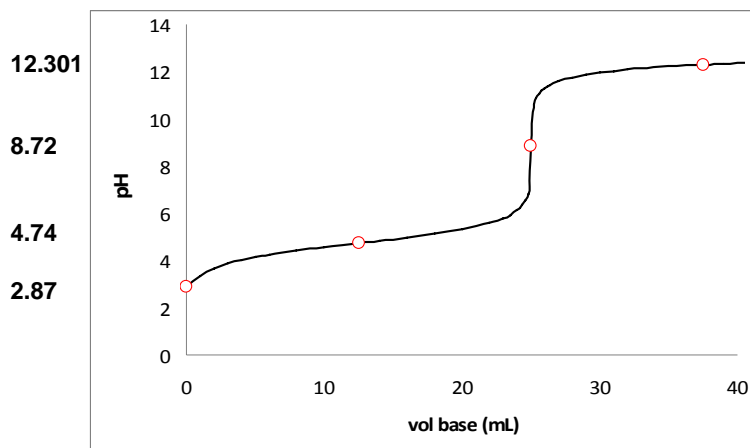


Strong Acid – Strong Base

- 4 points calculated:



Weak Acid – Strong Base Titration

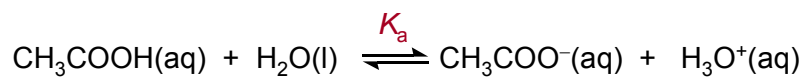




- Titrate 25.0 mL 0.100 M $\text{CH}_3\text{COOH}(\text{aq})$ with 0.100 M $\text{NaOH}(\text{aq})$

Practice Calculations: Weak Acid – Strong Base

0 mL NaOH = only weak acid present

- Solve pH of weak acid, use K_a



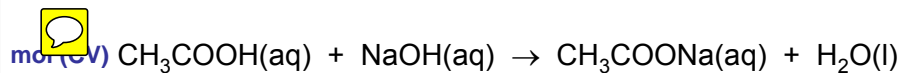
| | | | |
|---------|---|---|---|
| Initial |  |  |  |
| Change |  |  |  |
| Eqm |  |  |  |



Practice Calculations: Weak Acid – Strong Base

12.5 mL NaOH = ½-equivalence point 

- ½ CH₃COOH consumed.



Before



After



Practice Calculations: Weak Acid – Strong Base

Solve for pH of a buffer with use of an ICE table or the Henderson-Hasselbalch equation (below)...more on this to come.

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right)$$

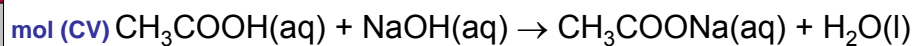
=  

pH = pK_a at ½-equivalence point of a weak-strong titration

Practice Calculations: Weak Acid – Strong Base

25.0 mL NaOH = equivalence point 

- All CH₃COOH consumed.



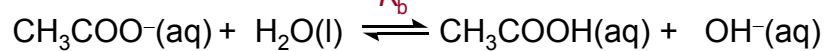
Before



After



Practice Calculations: Weak Acid – Strong Base



Initial



Change

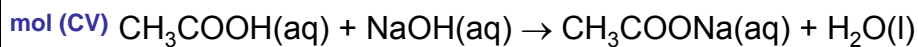
Eqm



Practice Calculations: Weak Acid – Strong Base

37.5 mL NaOH = only strong base present

- All CH_3COOH consumed; excess NaOH.



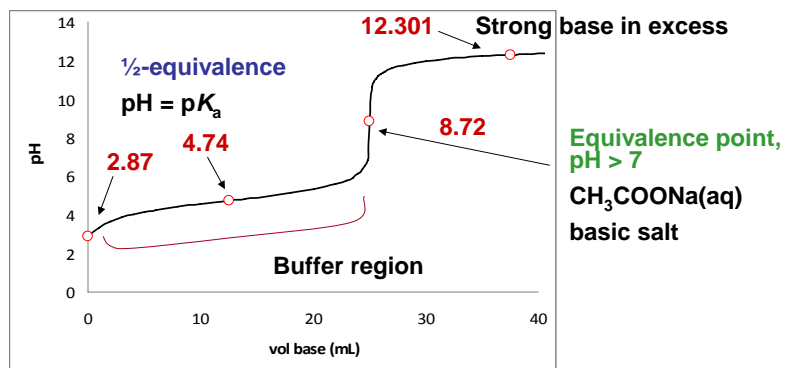
Before



After



Weak Acid – Strong Base Titration



- Features different from strong acid-strong base:

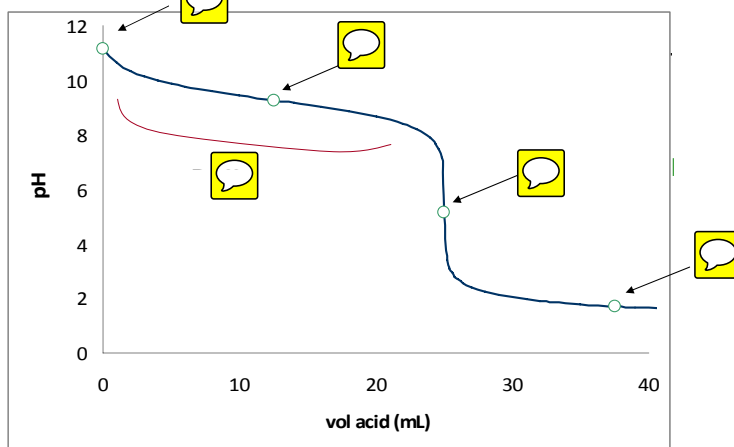


iClicker #1






Weak Base – Strong Acid



Label the key features on the weak base-strong acid titration curve.



Titration – Key Concepts

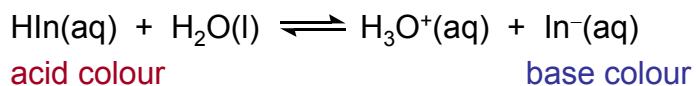
- Equivalence point: 
- Strong acid-strong base titration 
- Weak acid-strong base / strong acid-weak base titrations 

17.3 Acid-Base Indicators

- Equivalence point: theoretical point where mol acid = mol base (1:1 titration) 
- With an indicator, we observe the **endpoint** (colour change) 

Acid-Base Indicators

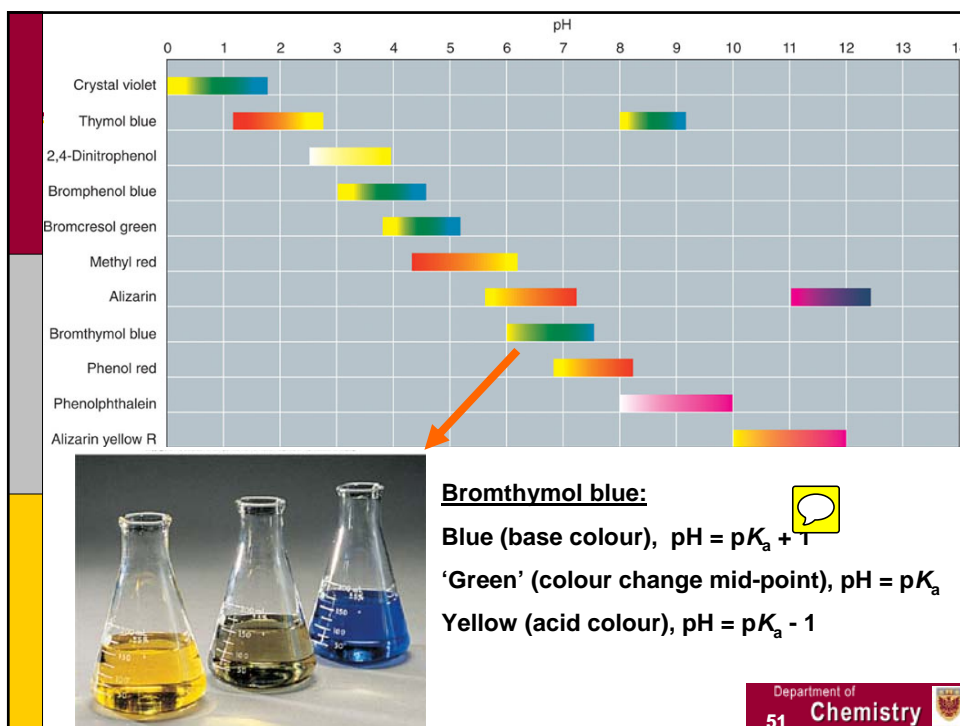
- Colour depends on pH
- Indicators are weak acids/bases (HIn , In^-):




- Eq. 17.4 relates solution pH to $\text{p}K_a$ of indicator


Acid-Base Indicators

- We see:
 - acid colour when $\text{pH} < (\text{p}K_{\text{HIn}} - 1)$ (10-fold excess of HIn)
 - base colour when $\text{pH} > (\text{p}K_{\text{HIn}} + 1)$ (10-fold excess of In^-)
- Colour change over ~ 2 pH units
- Want the colour change to be at or close to* the equivalence point
- How to choose a suitable indicator?



iClicker #2, #3



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Indicators - Key concepts



Buffers & Titrations

- Where do we see the importance of buffers?
 - Patients' blood pH (e.g., acidosis)
 - Biochemical assays
 - Lakes and streams
- How do we control buffer pH?
 - With addition of appropriate acid or base

The chemistry of a buffer

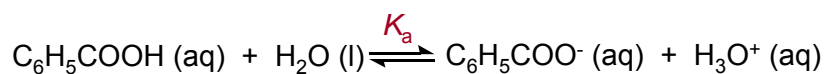
- Buffer chemistry: *equilibrium* reaction of either weak species with water (e.g. $\text{NH}_3/\text{NH}_4^+$):



- Looks like weak base or weak acid ionization in water, but now weak base **and** weak acid concentrations are both significant.

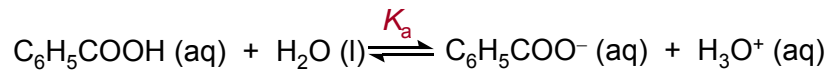
17-1: Common Ion Effect


0.10 M $\text{C}_6\text{H}_5\text{COOH}$ has pH 2.60 and is 2.5% ionized (slide 13).



Concept check: What would be the effect on the **pH** and on the **% ionization** of 0.10 M benzoic acid solution with the addition of $\text{C}_6\text{H}_5\text{COONa}(\text{aq})$?

Concept Check: Common Ion Effect




Add $\text{C}_6\text{H}_5\text{COO}^-$:



- Adding $\text{C}_6\text{H}_5\text{COO}^-$ (aq) to $\text{C}_6\text{H}_5\text{COOH}$ (aq) produces a **buffer solution** – an equilibrium mixture of a weak conjugate acid-base pair

17-2 Buffers: Applying the Common Ion Effect

- A buffer solution is:
 - a solution of a weak acid-base conjugate pair and
 - both concentrations $> 100 \times K_a$

- Buffer capacity:
 - a buffer is effective when:



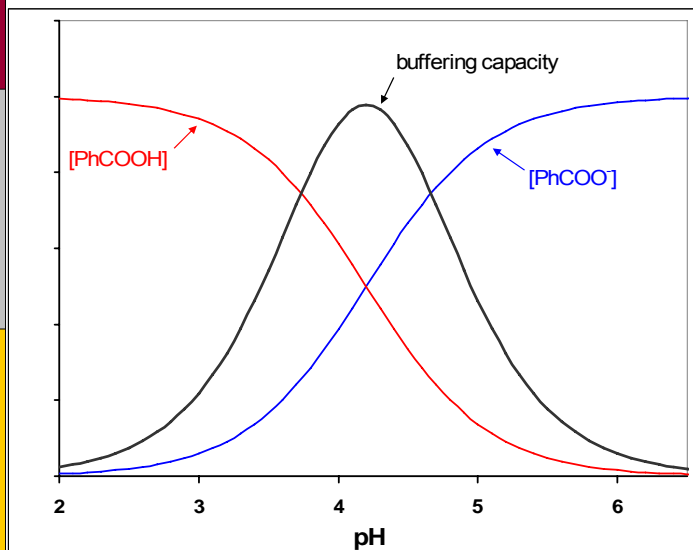
(eq. 17.3)

- best when [weak acid] & [weak base] are **large** and **equal**

Buffer Capacity



- Buffer capacity: maximum at equal $[\text{PhCOOH}]$ and $[\text{PhCOO}^-]$



Effective range
 $\text{pH} = \text{p}K_a \pm 1$

$\text{PhCOOH} =$
benzoic acid
 $\text{PhCOO}^- =$
benzoate ion

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How to make a buffer – 3 ways

1. Mix weak conjugate acid & base together

e.g.,

2. Titrate a **weak acid** with a limiting amount of **STRONG BASE** (to produce the conjugate **weak base**)

e.g.,

3. Titrate a **weak base** with a limiting amount of **STRONG ACID** (to produce the conjugate **weak acid**)

e.g.,


See Fig. 17-6

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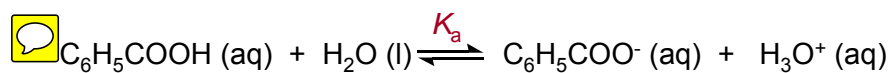
iClicker #4



Calculate pH of buffer from K_a (or K_b)

- Calculate pH & % ionization for 250. mL of a solution of:
0.100 M $C_6H_5COOH(aq)$ and 0.0850 M $C_6H_5COONa(aq)$ 
- Write down the chemistry (start with weak acid or base).
- The conjugate weak acid-base pair do NOT react with each other; one of them reacts with H_2O .

Calculate pH of buffer from K_a (or K_b)



| | | | |
|---------|----------------------|----------------------|----------------------|
| Initial | <input type="text"/> | <input type="text"/> | <input type="text"/> |
| Change | <input type="text"/> | <input type="text"/> | <input type="text"/> |
| Eq'm | <input type="text"/> | <input type="text"/> | <input type="text"/> |



Calculate pH of buffer from K_a (or K_b)

The common ion suppresses acid ionization, so we can ignore the "+ x" and "- x" terms:

$$\frac{[\text{HA}]}{K_a} = \frac{0.100}{6.3 \times 10^{-5}} = 1.6 \times 10^3, \text{ which is } > 100$$

...continued

Calculate buffer pH from K_a (or K_b)

pH = .

pH **increased** compared to solution of C_6H_5COOH only, where pH = 2.60 (slide 13)

% ionization

$$\frac{[H_3O^+]}{[HA]_{\text{initial}}} \times 100 = .$$

Buffer ionization **decreased** vs. C_6H_5COOH only, where ionization was 2.5 %

∴ We can ignore ionization in a buffer! (i.e., the small x approximation is always valid in a buffer)

Alternative calculation of Buffer pH: Henderson-Hasselbalch Equation

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

Rearrange to get:



Take “-log” of all terms:

Alternative calculation of Buffer pH: Henderson-Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}\right)$$

Or, more generally:



→ Henderson-Hasselbalch
equation (**eq. 17.2**)

In our example,



What does a buffer do?

- Resist changes in pH, to the limit of buffer capacity.
- Demonstration: Addition of acid and base to water vs. pH 7 buffer

Effect of adding strong acid or base?

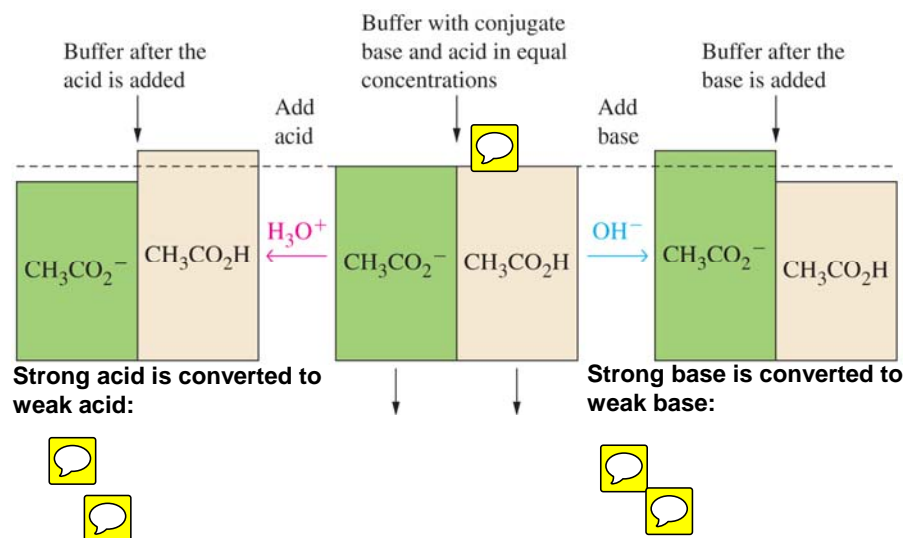


Fig. 17-5

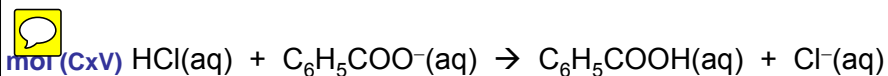
iClicker #5



Example: Buffer + Strong Acid

Add 20.0 mL of 0.150 M HCl(aq) to our buffer. What is pH?
 (Buffer = 250. mL of 0.100 M C₆H₅COOH(aq) and 0.0850 M NaC₆H₅COO(aq)).

- The strong acid will react with the basic component of the buffer:



Before

After

See also Ex. 17-6

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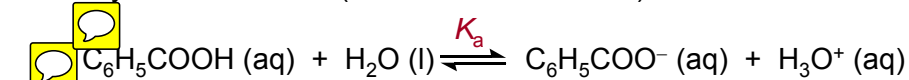
Buffer + Strong Acid

Concept check: Does Cl⁻(aq) impact pH?

No – so we will not include it in our calculations. (It is a spectator).

New concentrations:

divide by TOTAL volume (250. + 20.0 = 270. mL)



Initial

Change

Eq'm

Solve for pH with K_a or Henderson-Hasselbalch

Department of
72 Chemistry

Buffer + Strong Acid

K_a :

$$6.3 \times 10^{-5} = \frac{(0.0676 + x)(x)}{(0.104 - x)}$$



Henderson-Hasselbalch:


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




Buffer Change

Concept check: What is the effect on pH of our buffer if:

Add small amount NaOH?  

Add large amount of NaOH? 

Add small amount of water? 

iClicker #6, #7



See Ex. 17-5

Buffers: Key Concepts



Buffers Key Concepts



Trauma, Critical Care & pH Monitoring



- Blood pH (7.4) is a highly regulated parameter of physiology



- Acidosis of blood (pH < 7.35) can be triggered in cases of acute infection (sepsis), cardiac arrest or pulmonary dysfunction (hypoxia)

- Blood pH < 6.8 or > 7.8 is fatal.

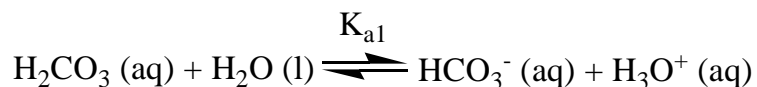
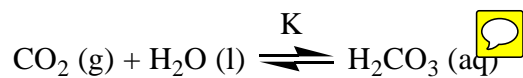
- Blood pH regulated by primarily by volatile CO₂ & non-volatile acids, such as bicarbonate, phosphate, lactate, protein etc.



Blood pH

- Equations:

Two-step dissolution & ionization equilibria

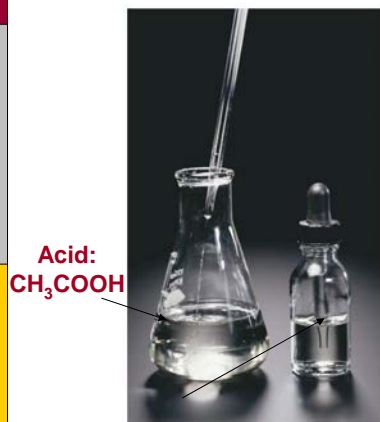


Net Reaction



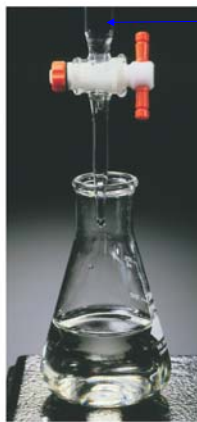
Titration that Saves Lives!

Persistent cases of **acidosis** treated with **bicarbonate** infusion (NaHCO_3) to prevent total organ failure → **Titration!**



Acid:
 CH_3COOH

Chemical Indicator
Phenolphthalein

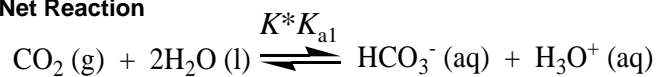


Base: NaOH



Persistent Acidosis: Treatment

Net Reaction



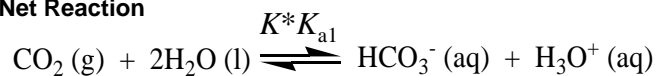
$$K^*K_{a1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{P_{\text{CO}_2}}$$

• multiply by -log



Persistent Acidosis: Treatment

Net Reaction



$$pK + pK_{a1} = -\log \frac{[\text{HCO}_3^-]}{P_{\text{CO}_2}} + pH$$

$pK_{a1} = 6.35$ $pK = 1.47$

$$\frac{[\text{HCO}_3^-]}{P_{\text{CO}_2}} = 10^{(pH - pK_{a1} - pK)}$$

Homeostasis, pH = 7.4 $\rightarrow \frac{[\text{HCO}_3^-]}{P_{\text{CO}_2}} \approx 0.38$

Acidosis, pH = 6.4 $\rightarrow \frac{[\text{HCO}_3^-]}{P_{\text{CO}_2}} \approx 0.038$



Impact of Titration
with NaHCO_3 ?