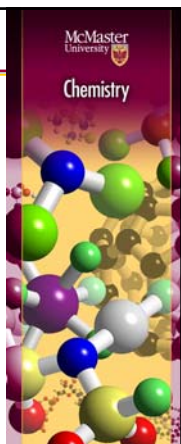


Acid-Base Chemistry

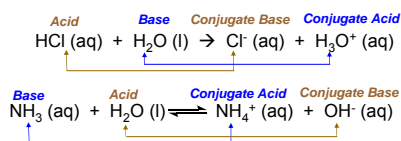
Ch. 17: Additional Aspects of Acid-Base Equilibria



Acid-Base Chemistry: Review (Ch 16)

Brønsted-Lowry Theory

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



- H_2O is an **amphoteric** species (behaves as both an acid or a base)

Refer to Ch. 16-2

Department of
Chemistry

Review: Strong Acids/Bases vs. Weak

- **Strong acids to know (6):**
HCl, HBr, HI, $HClO_4$, HNO_3 , H_2SO_4
- **Strong bases to know:**
Grp I & Grp II hydroxides (many Grp II partially soluble), hydrides (H^-) & oxides (O^{2-})

Refer to Ch 16-4

Department of
Chemistry

Review: Strong Acids/Bases vs. Weak

Concept Check:

- What is the difference between a strong acid (or base) and a weak acid (or base)?
- Give an example of: a weak acid, a weak base.
- How do you identify whether an acid or base is weak?

Refer to Ch 16-4

Department of
Chemistry

Review: Strong Acids/Bases vs. Weak

Concept check:

- Weak acids/bases** undergo **partial ionization** in water; **strong acids/bases** undergo **~complete ionization** in water
- Weak acids: **Carboxylic acids**, HF, H_2CO_3 , H_2SO_3 , $HClO_2$, ...
Weak bases: **Amines**, NH_3 , CO_3^{2-} , ...

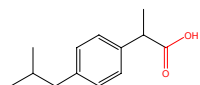
Refer to Ch 16-5

Department of
Chemistry

Review: Strong Acids/Bases vs. Weak

Concept check:

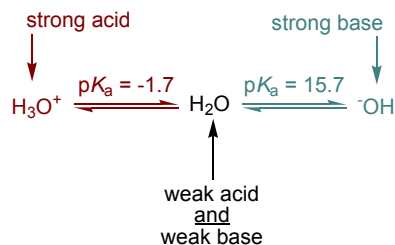
- Extent of ionization** described in by K_a or K_b
 - weak acid: $K_a < 1$ or $pK_a > 0$
 - weak base: $K_b < 1$ or $pK_b > 0$

Ibuprofen, pK_a 4.4, weak acid

Refer to Ch 16-5

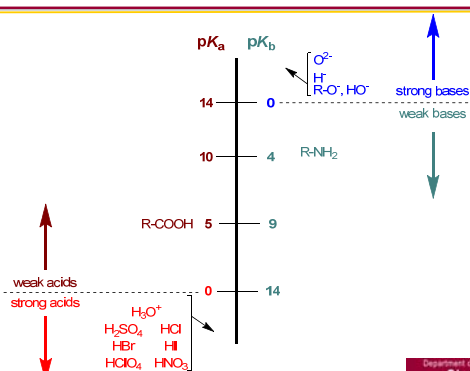
Department of
Chemistry

Review: Water is Amphoteric



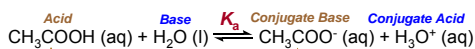
Department of Chemistry

Review: Typical pK_a Values



Department of Chemistry

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:

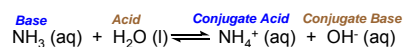
Acidity of $\text{H}_3\text{O}^+ > \text{CH}_3\text{COOH}$

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

Refer to Ch 16-5

Department of Chemistry

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:

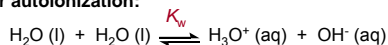
Basicity of $\text{OH}^- > \text{NH}_3$

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

Department of Chemistry

Review of relationships we know: pH and pK_w

Water autoionization:



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

$$\boxed{pK_w = \text{pH} + \text{pOH} = 14.0} \text{ Aqueous solution}$$

For a conjugate acid-base pair:

$$\boxed{pK_a + pK_b = pK_w = 14.0}$$

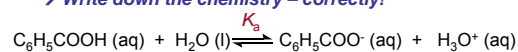
For help with these concepts, see the acid-base podcasts in Avenue, and in Petrucci refer to Ch 16-3 and 16-7

Department of Chemistry

Review: Weak Acids/Bases: Assumptions

Determine the pH and % ionization of a 0.100 M solution of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$): $K_a = 6.3 \times 10^{-5}$

→ 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

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{x^2}{0.100 - x} = 6.3 \times 10^{-5}$$

Assume $x \ll 0.100$, then $(0.100 - x) \approx 0.100$

Refer to Ex 16-6

Department of Chemistry

Review: Weak Acids/Bases: Assumptions

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

Check: If $\frac{[HA]}{K_a} > 100$ then assumption is valid (< 5% error):
 $\frac{0.100}{6.3 \times 10^{-5}} = 1.6 \times 10^3$, which is > 100

Then: $x^2 = (0.100)(6.3 \times 10^{-5})$; $x = [H_3O^+] = 2.5_1 \times 10^{-3}$

and: **pH = $-\log(2.5_1 \times 10^{-3}) = 2.60$**

% Ionization

$$\frac{[A^-]}{[HA]_{\text{initial}}} \times 100 = \frac{2.51 \times 10^{-3} \text{ M}}{0.100 \text{ M}} \times 100 = \boxed{2.51\%}$$

Department of
13 Chemistry

Diagnostic iClicker question

What is the pH of 0.1 M LiCl(aq)?

- (a) 7.0
- (b) 9.0
- (c) 3.8
- (d) 12.0
- (e) Need more information.

Department of
14 Chemistry

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:

$\text{NaCl (aq)} \rightarrow \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$ • but what happens to the ions?

$\text{Na}^+ \text{ (aq)} + \text{H}_2\text{O (l)} \rightarrow \text{No Reaction}$ Neither ion reacts with H_2O

$\text{Cl}^- \text{ (aq)} + \text{H}_2\text{O (l)} \rightarrow \text{No Reaction}$ ∴ pH = 7 (Neutral)

Department of
15 Chemistry

Review: pH of Salt Solutions

Is the pH of 0.1 M $\text{NH}_4\text{Cl(aq)}$ acidic, basic, or neutral?

$\text{NH}_4\text{Cl (aq)} \rightarrow \text{NH}_4^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$ • salt dissolves

$\text{Cl}^- \text{ (aq)} + \text{H}_2\text{O (l)} \rightarrow \text{No Reaction}$

$\text{NH}_4^+ \text{ (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{NH}_3 \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)}$

pH < 7 (acidic)

Department of
16 Chemistry

Review: pH of Salt Solutions

Is the pH of 0.1 M $\text{CH}_3\text{COONa (aq)}$ acidic, basic or neutral?

$\text{CH}_3\text{COONa (aq)} \rightarrow \text{Na}^+ \text{ (aq)} + \text{CH}_3\text{COO}^- \text{ (aq)}$ • salt dissolves

$\text{Na}^+ \text{ (aq)} + \text{H}_2\text{O (l)} \rightarrow \text{No Reaction}$

$\text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{OH}^- \text{ (aq)} + \text{CH}_3\text{COOH (aq)}$

pH > 7 (alkaline)

Department of
17 Chemistry

Acid-Base Review

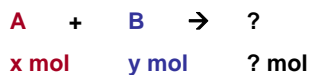
• Key concepts

- Brønsted-Lowry acid = H^+ donor, base = H^+ acceptor
- Conjugate acid-base pairs
- Strong acids/bases: ~100% ionized in water
- Weak acids/bases: equilibrium reaction with water
 - K_a and K_b values
- pH of weak acid or weak base = equilibrium calculation
- $\text{pH} + \text{pOH} = 14$ for an aqueous solution
- $\text{p}K_a + \text{p}K_b = 14$ for a conjugate acid-base pair
- pH of salt: acidic, neutral or basic

Department of
18 Chemistry

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



Department of
19 Chemistry

Acid-Base Reactions

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

Department of
20 Chemistry

1. STRONG BASE + STRONG ACID

Limiting reagent: consider **moles** before & after reaction.

Stoichiometry (mole) table:

mol	NaOH(aq)	+ HCl(aq)	→ NaCl(aq)	+ H ₂ O(l)
Before	0.85	0.60	-	
After	0.25	0	0.60	
	STRONG BASE	Limiting reagent (consumed)	neutral salt	

The solution that remains is **STRONG BASE**.

Department of
21 Chemistry

1. STRONG BASE + STRONG ACID



Before	1.3	1.3	-
After	0	0	1.3
	Limiting reagents (both are consumed)		neutral salt

The solution that remains is neutral (pH = 7).

Department of
22 Chemistry

1. STRONG BASE + STRONG ACID



Before	1.2	1.6	-
After	0	0.4	1.2
	Limiting reagent (consumed)	STRONG ACID	neutral salt

The solution that remains is **STRONG ACID**.

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = \frac{\text{mol STRONG ACID remaining}}{\text{total solution volume}}$$

Department of
23 Chemistry

2. STRONG BASE + weak acid



Before	1.3	0.80	-
After	0.50	0	0.80
	STRONG BASE	Limiting reagent (consumed)	weakly basic salt

The solution that remains is **STRONG BASE**.

pH is determined only from the **STRONG BASE**.

$$\text{pH} = 14 - \text{pOH}$$

Department of
24 Chemistry

2. STRONG BASE + weak acid



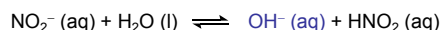
Before	1.1	1.1	-
After	0	0	1.1

Limiting reagents
(both are consumed)

weakly
basic salt

The solution that remains is **weakly basic**.

pH is calculated as that of a **weak base** solution.



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25 Chemistry

2. STRONG BASE + weak acid



Before	0.80	1.3	-
After	0	0.5	0.80

Limiting reagent
(consumed)

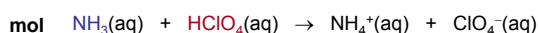
weak
acid

weakly
basic salt

The solution that remains is a mixture of a **weak acid** and its conjugate **weak base**. This is a special case – a **buffer** solution.

Department of
26 Chemistry

3. weak base + STRONG ACID



Before	0.60	0.85	-
After	0	0.25	0.60

Limiting reagent
(consumed)

STRONG
ACID

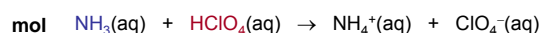
weakly
acidic ion

The solution that remains is **STRONG ACID**.

pH is determined only from the **STRONG ACID**.

Department of
27 Chemistry

3. weak base + STRONG ACID



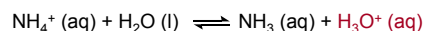
Before	0.75	0.75	-
After	0	0	0.75

Limiting reagents
(both are consumed)

weakly
acidic ion

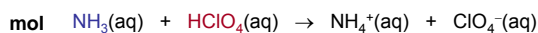
The solution that remains is **weakly acidic**.

pH is calculated as that of a **weak acid** solution.



Department of
28 Chemistry

3. weak base + STRONG ACID



Before	0.85	0.60	-
After	0.25	0	0.60

weak
base

Limiting reagent
(consumed)

weakly
acidic salt

The solution that remains is a mixture of a **weak base** and its conjugate **weak acid**. This is a special case – a **buffer** solution.

Department of
29 Chemistry

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 → neutral salt → strong base

Weak Acid + Strong Base

weak acid → buffer → basic salt → strong base

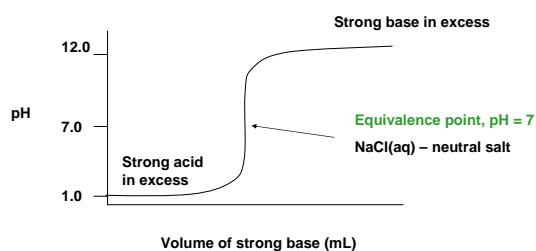
Weak Base + Strong Acid

weak base → buffer → acidic salt → strong acid

- Not covered: weak acid + weak base.

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30 Chemistry

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



Department of
31 Chemistry

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 $[H_3O^+] = [HCl]$

$$pH = -\log[H_3O^+] = -\log(0.100) = 1.000$$

Department of
32 Chemistry

Practice Calculations: Strong Acid – Strong Base

12.5 mL NaOH = $\frac{1}{2}$ -equivalence point

- $\frac{1}{2}$ of HCl consumed.

mol (CV)	HCl(aq)	NaOH(aq)	NaCl(aq)	H ₂ O(l)
Before	2.50×10^{-3}	1.25×10^{-3}	0	-
After	1.25×10^{-3}	0	1.25×10^{-3}	

- NaCl does not affect pH.
- Some HCl(aq) remains – in a new TOTAL volume.
 $pH = -\log[H_3O^+] = -\log(1.25 \times 10^{-3} \text{ mol} / 0.0375 \text{ L}) = 1.477$

Department of
33 Chemistry

Practice Calculations: Strong Acid – Strong Base

25.0 mL NaOH = equivalence point

- All HCl consumed.

mol (CV)	HCl(aq)	NaOH(aq)	NaCl(aq)	H ₂ O(l)
Before	2.50×10^{-3}	2.50×10^{-3}	0	-
After	0	0	2.50×10^{-3}	

- NaCl does not affect pH.

$$pH = 7.000$$

Department of
34 Chemistry

Practice Calculations: Strong Acid – Strong Base

37.5 mL NaOH = only strong base present

- All HCl consumed; excess NaOH.

mol (CV)	HCl(aq)	NaOH(aq)	NaCl(aq)	H ₂ O(l)
Before	2.50×10^{-3}	3.75×10^{-3}	0	-
After	0	1.25×10^{-3}	2.50×10^{-3}	

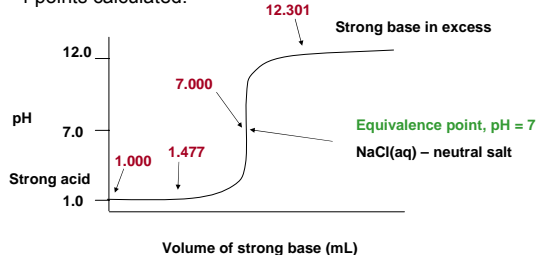
$$pOH = -\log[OH^-] = -\log(1.25 \times 10^{-3} \text{ mol} / 0.0625 \text{ L}) = 1.699$$

$$pH = 14 - pOH = 12.301$$

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35 Chemistry

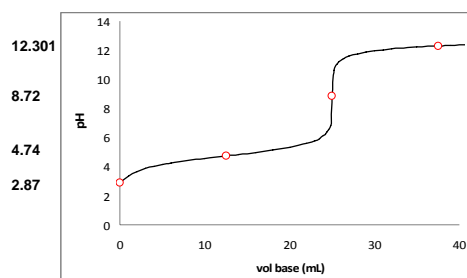
Strong Acid – Strong Base

- 4 points calculated:



Department of
36 Chemistry

Weak Acid – Strong Base Titration



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

Department of Chemistry

Practice Calculations: Weak Acid – Strong Base

0 mL NaOH = only weak acid present

- Solve pH of weak acid, use K_a

$$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{K_a} \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

Initial	0.100 M	-	0 M	0 M
Change	- x M		+ x M	+ x M
Eqm	0.100 - x M		x M	x M

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

$$x = [\text{H}_3\text{O}^+] = 1.34 \times 10^{-3}$$

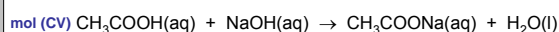
$$\text{pH} = -\log(1.34 \times 10^{-3}) = 2.87$$

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Practice Calculations: Weak Acid – Strong Base

12.5 mL NaOH = $\frac{1}{2}$ -equivalence point

- $\frac{1}{2}$ CH_3COOH consumed.



Before	2.50×10^{-3}	1.25×10^{-3}	0	-
After	1.25×10^{-3}	0	1.25×10^{-3}	

- CH_3COONa is a basic salt, and does affect pH.
- Some CH_3COOH remains.
- This is a **BUFFER!**

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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.

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

$$= 4.74 + \log \left(\frac{1.25 \times 10^{-3} \text{ mol} / 0.0375 \text{ L}}{1.25 \times 10^{-3} \text{ mol} / 0.0375 \text{ L}} \right) = 4.74$$

$$\text{pH} = \text{p}K_a \text{ at } \frac{1}{2}\text{-equivalence point of a weak-strong titration}$$

Department of Chemistry

Practice Calculations: Weak Acid – Strong Base

25.0 mL NaOH = equivalence point

- All CH_3COOH consumed.



Before	2.50×10^{-3}	2.50×10^{-3}	0	-
After	0	0	2.50×10^{-3}	

- CH_3COONa is a **basic salt**, and does affect pH.

Solve for the pH of a weak base:

$$[\text{CH}_3\text{COO}^-] = 2.50 \times 10^{-3} \text{ mol} / 0.0500 \text{ L} = 0.0500 \text{ M}$$

Department of Chemistry

Practice Calculations: Weak Acid – Strong Base

$$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{K_b} \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$$

Initial	0.050 M	-	0 M	0 M
Change	- x M		+ x M	+ x M
Eqm	0.050 - x M		x M	x M

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.050 - x} = \frac{K_w}{K_a} = 5.56 \times 10^{-10}$$

$$x = [\text{OH}^-] = 5.27 \times 10^{-6}, \quad \text{pOH} = -\log [\text{OH}^-] = 5.28$$

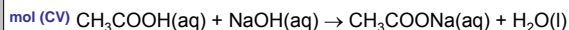
$$\text{pH} = 14 - \text{pOH} = 8.72$$

Department of Chemistry

Practice Calculations: Weak Acid – Strong Base

37.5 mL NaOH = only strong base present

- All CH_3COOH consumed; excess NaOH.



Before	2.50×10^{-3}	3.75×10^{-3}	0	-
After	0	1.25×10^{-3}	2.50×10^{-3}	

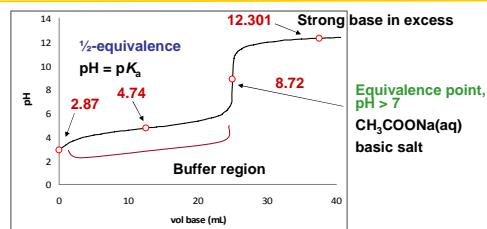
Excess strong base and weak base: strong base determines pH.

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.25 \times 10^{-3} \text{ mol} / 0.0625 \text{ L}) = 1.699$$

$$\text{pH} = 14 - \text{pOH} = 12.301$$

Department of
43 Chemistry

Weak Acid – Strong Base Titration

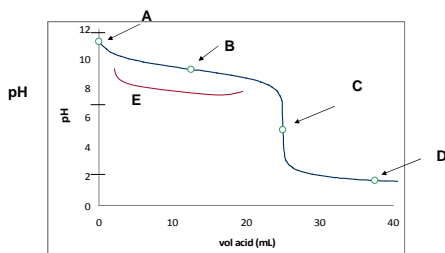


- Features different from strong acid-strong base:
 Start at higher pH
 Buffer region
 $\frac{1}{2}$ -equivalence point, $\text{pH} = \text{pK}_a$
 Equivalence point $\text{pH} > 7$

Department of
44 Chemistry

iClicker #1

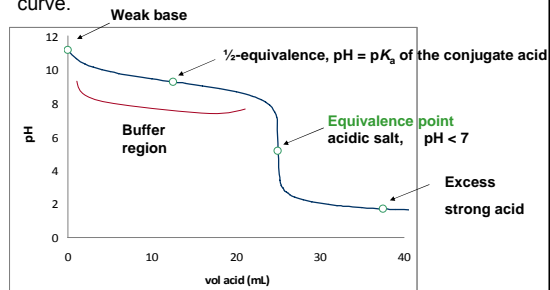
Which label shows where $\text{pH} = \text{pK}_a$ point on this titration curve?



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45 Chemistry

Weak Base – Strong Acid

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



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46 Chemistry

Titration – Key Concepts

- Equivalence point: mol acid = mol base (if 1:1 reaction)
- Strong acid-strong base titration
 - $\text{pH} = 7$ at equivalence point
 - Sharp pH change at equivalence
- Weak acid-strong base / strong acid-weak base titrations
 - Buffer region
 - $\text{pH} = \text{pK}_a$ at $\frac{1}{2}$ -equivalence
 - $\text{pH} \neq 7$ at equivalence (pH depends on the salt present – acidic or basic)

Department of
47 Chemistry

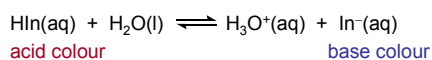
17.3 Acid-Base Indicators

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

Department of
48 Chemistry

Acid-Base Indicators

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

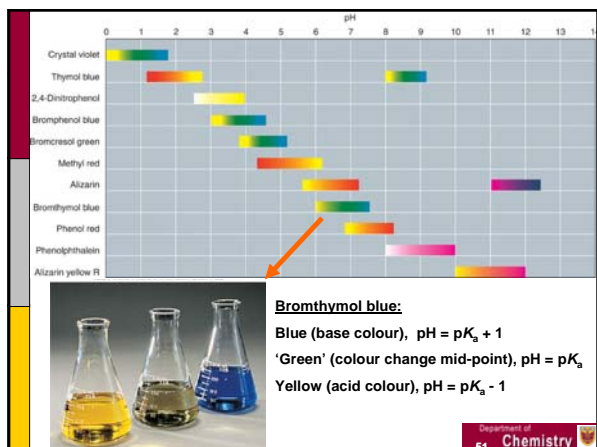


$$K_{\text{HIn}} = \frac{[\text{In}^-][\text{H}_3\text{O}^+]}{[\text{HIn}]} \quad \text{or} \quad \text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad (17.4)$$

- Eq. 17.4 relates solution pH to $\text{p}K_{\text{a}}$ 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?
 - Select an indicator with $\text{p}K_{\text{a}}$ ($\text{p}K_{\text{HIn}}$) close to expected equivalence point pH



iClicker #2, #3

- From the following list indicators, select a suitable indicator for the titration of
 - (1) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq})$
 - (2) $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq})$

Indicator	Colour change range (pH)
(A) Methyl violet	0.1 – 1.7
(B) Bromocresol green	4.0 – 5.8
(C) Phenol red	6.3 – 8.0
(D) Alizarin yellow-R	10.0 – 12.0

Indicators - Key concepts

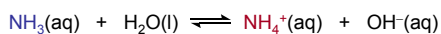
- Indicators are weak acids/bases
- Colour changes from acid to base form
- Colour change occurs over ~ 2 pH units
- Choose indicator with $\text{p}K_{\text{a}}$ close to pH of titration equivalence point

Buffers & Titrations

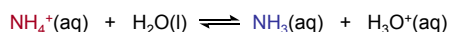
- Where do we see the importance of buffers?
 - Patients' blood pH (e.g., acidosis)
 - Biochemical assays
 - Lakes and streams
- How do we control buffer pH?
 - With addition of appropriate acid or base

The chemistry of a buffer

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



- and -

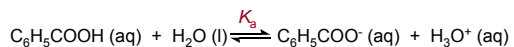


- Looks like weak base or weak acid ionization in water, but now weak base **and** weak acid concentrations are both significant.

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55 Chemistry

17-1: Common Ion Effect

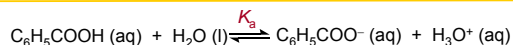
0.10 M $\text{C}_6\text{H}_5\text{COOH}$ has pH 2.60 and is 2.5% ionized (slide 13).



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 $\text{C}_6\text{H}_5\text{COONa}(\text{aq})$?

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Concept Check: Common Ion Effect



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

Equilibrium shifts left

Ionization decreases

pH increases (we added a weak base!)

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

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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:

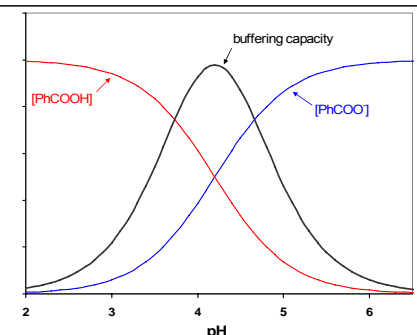
$$0.1 < \frac{[\text{weak base}]}{[\text{weak acid}]} < 10 \quad (\text{eq. 17.3})$$

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

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Buffer Capacity

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



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

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How to make a buffer – 3 ways

1. Mix weak conjugate acid & base together

e.g., HCOOH and HCOONa
 NH_3 and NH_4Cl

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

e.g., $\text{HCOOH} + \text{NaOH}$
 $\text{NH}_4\text{Cl} + \text{NaOH}$

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

e.g., $\text{HCOONa} + \text{HCl}$
 $\text{NH}_3 + \text{HCl}$

See Fig. 17-6

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60 Chemistry

iClicker #4

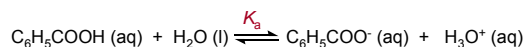
Which combination of 1 M solutions will give a buffer?

- (A) 50 mL HCl + 50 mL NaOH
- (B) 50 mL HCl + 50 mL C₆H₅COOH
- (C) 50 mL NaOH + 50 mL C₆H₅COOH
- (D) 25 mL NaOH + 50 mL C₆H₅COONa
- (E) 25 mL NaOH + 50 mL C₆H₅COOH

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Calculate pH of buffer from K_a (or K_b)

- Calculate pH & % ionization for 250. mL of a solution of: 0.100 M C₆H₅COOH(aq) and 0.0850 M C₆H₅COONa (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 H₂O.



See also Ex. 17-2

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Calculate pH of buffer from K_a (or K_b)



Initial	0.100 M	-	0.0850 M	0 M
Change	- x M		+ x M	+ x M
Eq'm	0.100 - x M		0.0850 + x M	x M

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = 6.3 \times 10^{-5}$$

$$6.3 \times 10^{-5} = \frac{(0.0850 + x)(x)}{(0.100 - x)}$$

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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:

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

$$\text{Thus: } (0.100 - x) \approx 0.100 \\ (0.0850 + x) \approx 0.0850$$

$$\therefore 6.3 \times 10^{-5} = \frac{(0.085)(x)}{0.100} \\ x = 7.41 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

...continued

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Calculate buffer pH from K_a (or K_b)

$$\text{pH} = -\log [7.41 \times 10^{-5}] = 4.13$$

pH **increased** compared to solution of C₆H₅COOH only, where pH = 2.60 (slide 13)

% ionization

$$\frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_{\text{initial}}} \times 100 = \frac{7.41 \times 10^{-5} \text{ M}}{0.100 \text{ M}} \times 100 = 0.0741\% \text{ (negligible!)}$$

Buffer ionization **decreased** vs. C₆H₅COOH only, where ionization was 2.5 %

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

This is what we predicted (slide 57)

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Alternative calculation of Buffer pH: Henderson-Hasselbalch Equation

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

Rearrange to get:

$$[\text{H}_3\text{O}^+] = \frac{K_a [\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]}$$

Take "-log" of all terms:

$$-\log[\text{H}_3\text{O}^+] = -\log(K_a) - \log\left(\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]}\right)$$

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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:

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

→ Henderson-Hasselbalch equation (eq. 17.2)

In our example,

$$\text{pH} = 4.20 + \log \left(\frac{0.0850}{0.100} \right) = 4.13$$

SAME ANSWER as
'ICE' Table! (p. 65)

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67 Chemistry

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

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Effect of adding strong acid or base?

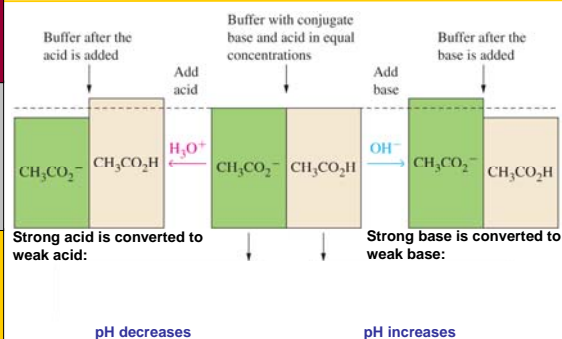
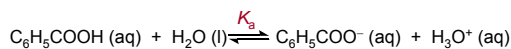


Fig. 17-5

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iClicker #5



When HCl(aq) is added to a benzoic acid/benzoate buffer (above), which of the following statements is/are TRUE?

- The equilibrium shifts left.
- $\text{C}_6\text{H}_5\text{COOH}$ ionization decreases.
- pH increases.

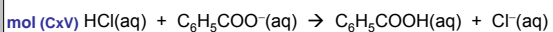
- (A) i (B) ii (C) iii
(D) i, ii (E) ii, iii

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70 Chemistry

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 $\text{C}_6\text{H}_5\text{COOH}$ (aq) and 0.0850 M $\text{NaC}_6\text{H}_5\text{COO}$ (aq)).

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



Before	3.00×10^{-3}	2.125×10^{-2}	2.50×10^{-2}	0
After	0	1.825×10^{-2}	2.80×10^{-2}	3.00×10^{-3}

We added a limiting amount of strong acid.

What remains is a buffer: $0.1 < \frac{[\text{weak base}]}{[\text{weak acid}]} < 10$

See also Ex. 17-6

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71 Chemistry

Buffer + Strong Acid

Concept check: Does $\text{Cl}^-(\text{aq})$ 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)

$$\text{C}_6\text{H}_5\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{K_a} \text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

Initial	0.104 M	-	0.0676 M	0 M
Change	- x M		+ x M	+ x M
Eq'm	0.104 - x M		0.0676 + x M	x M

Solve for pH with K_a or Henderson-Hasselbalch

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72 Chemistry

Buffer + Strong Acid

K_a :

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

Assume x is small.

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

$$x = 9.69 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = \underline{4.01}$$

Henderson-Hasselbalch:

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

$$\text{pH} = 4.20 + \log \left(\frac{0.0676}{0.104} \right)$$

$$\text{pH} = \underline{4.01}$$

pH decreased slightly (from 4.13) upon addition of a limiting amount of strong acid - as expected.

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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?

Small amount NaOH: pH **increases slightly**. Some benzoic acid is converted to benzoate ion.

Large amount NaOH: pH **increases a lot**. ALL of the benzoic acid is converted to benzoate ion, and possible excess NaOH remains. Buffer is destroyed.

Small amount of water: **no change in pH**. Moles of benzoic acid and benzoate ion are unchanged, and their concentrations are still sufficiently high.

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iClicker #6, #7

What acid would be the best choice to make a buffer of pH 5.5?

- | | |
|--|-----------------------|
| (A) HClO_2 | $\text{p}K_a = 1.96$ |
| (B) CH_3COOH | $\text{p}K_a = 4.74$ |
| (C) HOCl | $\text{p}K_a = 7.54$ |
| (D) NH_4Cl | $\text{p}K_a = 9.26$ |
| (E) $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Cl}$ | $\text{p}K_a = 10.84$ |

What reagent could be used to reach the correct pH?

- (A) NaOH
- (B) HCl

See Ex. 17-5

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75 Chemistry

Buffers: Key Concepts

- A buffer solution contains a weak conjugate acid-base pair with both concentrations $> 100 \times K_a$
- Buffer capacity:
 - a buffer is effective when: $0.1 < \frac{[\text{weak base}]}{[\text{weak acid}]} < 10$
 - best when [weak acid] & [weak base] are large and equal (maximum capacity)
- Buffer range: $\text{p}K_a \pm 1$

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Buffers Key Concepts

- Make a buffer:
 - Directly mix conjugate weak acid-base pair together
 - React weak acid with limiting amount of strong base
 - React weak base with limiting amount of strong acid
- Calculate buffer pH from K_a expression (or Henderson-Hasselbalch equation):

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$
- Buffers resist changes in pH by converting strong acid into weak acid, or strong base into weak base.

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Trauma, Critical Care & pH Monitoring

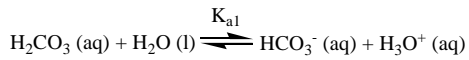
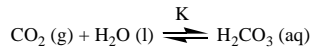
- Blood pH (7.4)** is a highly **regulated** parameter of physiology
- Acidosis** of blood ($\text{pH} < 7.35$) can be triggered in cases of acute infection (sepsis), cardiac arrest or pulmonary dysfunction (hypoxia)
- Blood pH < 6.8 or > 7.8 is fatal.
- Blood pH** regulated by primarily by **volatile CO_2** & non-volatile acids, such as bicarbonate, phosphate, lactate, protein etc.

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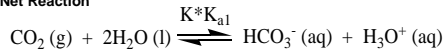
Blood pH

Equations:

Two-step dissolution & ionization equilibria



Net Reaction



$$K = 3.4 \times 10^{-2} (25^\circ\text{C})$$

$$K_{a1} = 4.5 \times 10^{-7} (25^\circ\text{C})$$

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Titration that Saves Lives!

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

Acid: CH_3COOH

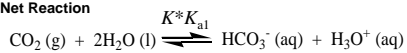
Base: NaOH

Chemical Indicator Phenolphthalein

$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

Persistent Acidosis: Treatment

Net Reaction



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

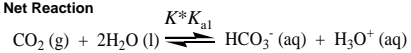
• multiply by -log

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

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Persistent Acidosis: Treatment

Net Reaction



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

$$pK_{s1} = 6.35 \quad pK = 1.47$$

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

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

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

Impact of Titration with NaHCO_3 ?

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