Acid/Base Chemistry

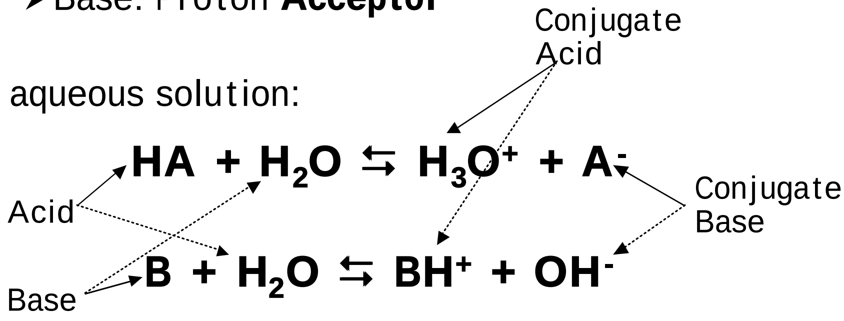
Chem 36

Spring 2002

Definitions

- ✓ **Bronsted-Lowry Model**
  - ➢ Acid: Proton *Donor*
  - ➢ Base: Proton **Acceptor**

In aqueous solution:



Conjugate Acid

$HA + H_2O \leftrightarrows H_3O^+ + A^-$

Acid

Conjugate Base

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

Base

Water

- Water can act *both* as an acid and as a base
  - *amphoteric*
- Water can react with *itself*
  - Auto-ionization or self-dissociation:

$$\mathbf{H_2O\ (l) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + OH^-\ (aq)}$$

$$K = \frac{[H_3O^+][OH^-]}{1} = \boxed{[H_3O^+][OH^-] = K_w}$$

1.0×10^{-14} at 25 °C

Water Equilibria

In pure water at 25 °C:

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

Substituting:

$$K_w = x^2 = 1.0 \times 10^{-14}$$

$$x = \underline{\mathbf{1.0 \times 10^{-7}}\ M} = [H_3O^+] = [OH^-]$$

Express small numbers as *logs:*

$$\boxed{\mathbf{pH = -Log[H_3O^+]}}$$

2 sig figs

So, for pure water at 25 °C:

$$pH = -Log(1.0 \times 10^{-7}) = \underline{\mathbf{7.00}}$$

Water Logged

- We can define other log functions:

$$pOH = -\mathrm{Log}[OH^-]$$

$$pK_w = -\mathrm{Log}K_w = \boldsymbol{\mathit{14.00}}$$

- We can quantify the *autoionization* of water entirely in logs:

$$\mathbf{pK_w = pH + pOH}$$

So, at 25 °C:

$$\boxed{\mathbf{pH + pOH = 14.00}}$$

Example

- What is the pH of an aqueous solution in which [OH-] = 1.0 x 10^{-10} *M* ?

$$K_w = [H^+][OH^-] \Rightarrow [H^+] = \frac{K_w}{[OH-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-10}} = 1.0 \times 10^{-4}\ M$$

So: $\mathbf{pH} = -\mathrm{Log}(1.0 \times 10^{-4}) = \underline{\boldsymbol{\mathit{4.00}}}$

It's easier with logs!

$$pOH = -\mathrm{Log}(1.0 \times 10^{-10}) = 10.00$$

So: $pH = 14.00 - pOH = 14.00 - 10.00 = \underline{\boldsymbol{\mathit{4.00}}}$

K_a and K_b

For *acid dissociation:*

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

We define an *acid dissociation constant:*

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

Similarly, for a *base:*

$$\mathbf{B\ (aq) + H_2O\ (l) \leftrightarrows BH^+\ (aq) + OH^-\ (aq)}$$

Where:

$$\boxed{K_b = \frac{[OH^-][BH^+]}{[B]}}$$

Acid (Base) *Strength*

- Magnitude of K_a (or K_b) indicates *degree of dissociation*
  - As K_a *increases,* the <u>degree of dissociation</u> *increases*
  - Increased dissociation = ***<u>more H</u>***
  - **<u>SO:</u>** as K_a increases, acid strength increases

<u>Example:</u>

Acetic Acid - CH_3COOH ($K_a \approx 10^{-5}$)
is *stronger* than
Hydrocyanic Acid - HCN ($K_a \approx 10^{-9}$)

Conjugate Acid/Base Pairs

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

$$\mathbf{A^-\ (aq) + H_2O\ (l) \leftrightarrows HA\ (aq) + OH^-\ (aq)}$$

$$\mathbf{H_2O\ (l) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + OH^-\ (aq)}$$

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

$$\boxed{K_a K_b = K_w} \text{ OR } \boxed{pK_w = pK_a + pK_b}$$

Conjugate A/B *Strengths*

- Sum of pK_a and pK_b always = 14.00 (at 25 °C)
- If an *acid* (HA) has a small pK_a, its **conjugate base** (A^-) will have a large pK_b
- Conjugate acid/base strengths are *complementary*

Example: **Acetic Acid**

$K_a = 1.76 \times 10^{-5}$

$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.76 \times 10^{-5} = 5.7 \times 10^{-10}$ (for Ac^-)

Strong versus Weak

- If $K_a >> 1$, acid is "completely" dissociated in water:

Strong Acid

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

Similarly for a base,

Strong Base

- If $K_b >> 1$, base dissociation is "complete":

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

Is the Conjugate Base of a Strong Acid, Strong or Weak?

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

conjugate base

What is K_b for Cl^-?

$K_b\ (Cl^-) = K_w/K_a\ (HCl)$

Substituting $K_a \approx 10^7$:

$K_b \approx 10^{-14}/10^7$

$K_b \approx 10^{-21}$

Cl^- is a *weaker base* than **H_2O**!
($K_b = K_w = 10^{-14}$)

Acid/Base Strength Depends on the Solvent

In water, HCl is a *strong acid:*

$HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$ $K_a \approx 10^7$

<u>So:</u>

- Cl^- is a *weaker base* than H_2O
- HCl is a *stronger acid* than H_3O^+

But, in <u>ether</u>, HCl is a *weak acid:*

$HCl\ (aq) + (CH_3CH_2)_2O\ (l) \leftrightarrows (CH_3CH_2)_2OH^+\ (aq) + Cl^-\ (aq)$ $K_a \ll 1$

<u>So:</u>

- Cl^- is a *stronger base* than ether
- HCl is a *weaker acid* than $(CH_3CH_2)_2OH^+$

The Leveling Effect

The *strongest acid* in any solvent is the <u>conjugate acid</u> of the solvent

- ➢ In water, the strongest acid is H_3O^+
- ➢ All acids that *dissociate completely* in water are ***leveled*** to the strength of H_3O^+
- ➢ All *strong acids* will seem *equally strong*

Can apply similar reasoning to base strengths

Example: NH_3 (l) as solvent

What is the strongest acid in an NH_3 (l) solvent?

$$NH_3\ (l) + NH_3\ (l) \leftrightarrows \underbrace{NH_4^+\ (aq)}_{\text{strongest acid}} + \underbrace{NH_2^-\ (aq)}_{\text{strongest base}}$$

In water, K_a of $NH_4^+ = K_w/K_b \approx 10^{-14}/10^{-5} = 10^{-9}$

of NH_3

➢So, any acids with a K_a in water > 10^{-9} will be *equally strong* ("leveled") in liquid ammonia

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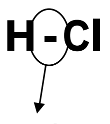
Effect of Structure on Acid/Base Strength

- Consider the following two compounds in an *aqueous* solution:

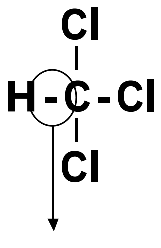


$H-Cl$

✓Polar bond

✓*Strong* Acid

versus



$H-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-Cl$

✓Nonpolar bond

✓*Not acidic*

Hypothesis: *Bond polarity* can be related to *acidity*

Bond Polarity versus Acidity

- Bond polarity for *hydrogen halides*:

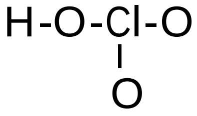
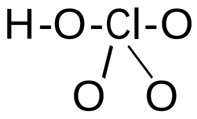
(most polar) H-F > H-Cl > H-Br > H-I (least polar)

	H-F	H-Cl	H-Br	H-I	
	565	427	363	295	kJ/mol
K_a =	10^{-3}	10^{7}	10^{9}	10^{11}	

➢But, *bond energies* increase with increasing polarity

➢So *acidity* decreases with increasing polarity

Oxyacid Acid Strengths

Oxyacid	**Structure**	**K_a**
HClO Hypochlorous Acid	H-O-Cl	3.5×10^{-8}
$HClO_2$ Chlorous Acid	H-O-Cl-O	1.2×10^{-2}
$HClO_3$ Chloric Acid	 $\mathrm{H{-}O{-}\underset{\underset{O}{\mid}}{Cl}{-}O}$	~1
$HClO_4$ Perchloric Acid	 $\mathrm{H{-}O{-}\underset{O\quad O}{\underset{/\ \ \backslash}{Cl}}{-}O}$	~10^{7}

In General

For compounds like:

H-O-X

- Increasing *electronegativity* of **X weakens** the H-O bond
- Increases compound acidity

➢ What if EN of **X** is *small?*

- O-X bond will be *ionic* and will dissociate in water:

H-O-**Na** ® **Na**$^+$ + OH$^-$ ***Base!***

Oxides

■ *Acidic* Oxides (covalent oxides)

$$SO_3\ (g) + H_2O\ (l) \rightarrow H_2SO_4\ (aq)$$
$$SO_2\ (g) + H_2O\ (l) \rightarrow H_2SO_3\ (aq)$$
$$CO_2\ (g) + H_2O\ (l) \rightarrow H_2CO_3\ (aq)$$

■ *Basic* Oxides (ionic oxides)

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (aq)$$
$$K_2O\ (s) + H_2O\ (l) \rightarrow 2KOH\ (aq)$$

$O^{2-}\ (aq) + H_2O\ (l) \rightarrow 2OH^-\ (aq)$

pH of Strong Acid solutions

Simple - Strong acids dissociate *completely*:

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

So, what's the pH of a ***0.10 M HCl*** solution?

C_{HCl} = 0.10 M, so:

$[H^+]$ = 0.10 *M* *(complete dissociation)*

solution concentration

pH = -Log(0.10) = ***1.00***

How about 1.0 x 10^{-10} *M* HCl?

As before:

$[H^+] = C_{HCl} = 1.0 \times 10^{-10}\ M$

pH = ***10.00***

Yikes! It's BASIC?!

Ooops! There are *TWO sources of H^+*:

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

and

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

$[H^+]$ from two reactions

So:

$$[H^+] = [H^+]_{HCl} + [H^+]_{H2O}$$

$$[H^+] = C_{HCl} + [OH^-]$$

$$[H^+] = C_{HCl} + K_w / [H^+]$$

It's a quadratic! Rearranging:

$$[H^+]^2 - C_{HCl}[H^+] - K_w = 0$$

On to the solution!

$$[H^+]^2 - \underset{1.0 \times 10^{-10}}{\underset{\uparrow}{C_{HCl}}}[H^+] - \underset{1.0 \times 10^{-14}}{\underset{\nwarrow}{K_w}} = 0$$

Solving for $[H^+]$, gives:

$[H^+] = 1.00050 \times 10^{-7}\ M$

pH = 6.99978 = ***<u>7.00</u>***

✓Autoionization of water is the *major source* of H^+ in this solution

Weak Acids - pH Calculation

- If we have K_a and solution concentration, this is just a straightforward equilibrium problem

Example: Calculate the pH of a 1.0×10^{-1} *M* **HF** solution ($K_a = 7.2. \times 10^{-4}$).

First, identify the major sources of H^+:

✓**HF** ← ***Major Source of*** H^+

✓**H_2O**

Safe to ignore:

- $K_a \gg K_w$
- C_{HF} is large

Apply *ICE*

$$HF\ (aq) \leftrightarrows H^+\ (aq) + F^-\ (aq)$$

	HF (aq)	H^+ (aq)	F^- (aq)
I	1.0×10^{-1} *M*	-	-
C	-x	+x	+x
E	$1.0 \times 10^{-1} - x$	x	x

Recall: $K_a = \dfrac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4}$

Substituting: $\boxed{\dfrac{x^2}{1.0 \times 10^{-1} - x} = 7.2 \times 10^{-4}}$

Quadratic Formula?

Rearranging:

$$x^2 + 7.2 \times 10^{-4}x - 7.2 \times 10^{-5} = 0$$

Substituting:

$$x = \frac{-7.2 \times 10^{-4} \pm 1.6986 \times 10^{-2}}{2}$$

Finally: $x = 8.1329 \times 10^{-3} = [H^+]$

pH = 2.0897 = ***2.09***

Successive Approximations?

$$\frac{x^2}{1.0 \times 10^{-1} - \mathbf{x}} = 7.2 \times 10^{-4}$$

Assume: $x \ll 1.0 \times 10^{-1}$

$$\frac{(x')^2}{1.0 \times 10^{-1}} = 7.2 \times 10^{-4}$$

$x' = 8.4853 \times 10^{-3}$

First approximation

$$\frac{(x'')^2}{1.0 \times 10^{-1} - 8.4853 \times 10^{-3}} = 7.2 \times 10^{-4}$$

2nd approx

$x'' = \mathbf{8.11730 \times 10^{-3}}$

4.5% change - *Stop!*

pH = ***2.09***

Successful Successive Approximations?

- **Assess Assumptions:**
  1. $[H^+] << 1.0 \times 10^{-1}$ *M*

     close . . . But should be *100x* difference
  2. We can ignore $[H^+]_{H2O}$
     - ✓ $[H^+] >> [H^+]_{H2O}$
- **When do we include** $[H^+]_{H2O}$?
  - ✓ *Dilute* solutions
  - ✓ *Very* weak ($K_a < 10^{-8}$) acids

What about Bases?

- Treat Bases *just like acids* **except:**
  - ✓Use K_b instead of K_a
  - ✓Calculate $[OH^-]$ first, convert to pOH
  - ✓Calculate pH from pOH
- ✓Examples
  - ✓pH of 0.10 *M* NaOH (strong base)
  - ✓pH of 0.10 *M* Methylamine (weak base) (CH_3NH_2 - $K_b = 4.38 \times 10^{-4}$)

Here's Another One!

- **Calculate the pH of a 0.10 *M* KCN solution** (K_a (HCN) = 6.2×10^{-10}).

What happens to KCN in water?

$$KCN \rightarrow K^+ + CN^-$$

conjugate base of HCN

So, the pH-determining species is a ***base***: CN^-

Find K_b for CN^-: $K_aK_b = K_w$ $K_b = K_w/K_a$

$$K_b = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = \mathbf{1.613 \times 10^{-5}}$$

ICE Table

	CN^- (aq) + H_2O (l)	$\leftrightharpoons$ HCN (aq)	+ OH^- (aq)
I	0.10	0	0
C	-x	+x	+x
E	0.10 - x	x	x

Substituting: $K_b = \frac{[HCN][OH^-]}{[CN^-]} = 1.613 \times 10^{-5}$

$$\boxed{\frac{x^2}{0.10 - x} = 1.613 \times 10^{-5}}$$

Quadratic Equation?

Successive Approximations?

Successive Approximations

$$\frac{x^2}{0.10 - x} = 1.613 \times 10^{-5}$$

Assume: $x \ll 0.10$

$$\frac{(x')^2}{0.10} = 1.613 \times 10^{-5}$$

First Approximation

$x' = 1.27 \times 10^{-3}$

$$\frac{(x'')^2}{0.10 - 1.27 \times 10^{-3}} = 1.613 \times 10^{-5}$$

2nd Approximation

$x'' = \underline{\mathbf{1.26 \times 10^{-3}}}$ ← Less than 1% change - ***Stop!***

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pH Please!

$[OH^-] = x = 1.26 \times 10^{-3}\ M$

$pOH = -\mathrm{Log}(1.26 \times 10^{-3}) = 2.899$

$pH = 14.00 - pOH = \underline{\mathbf{11.10}}$

- *Anions* of Weak Acids are Weak Bases
  - ✓ KCN in water will be basic
- **Cations** of Weak Bases are Weak Acids
  - ✓ NH_4NO_3 in water will be acidic

Common Ion Effect

- Suppose we add a *common ion* to a weak acid system at equilibrium?

Example: add *Sodium Acetate* to a solution of Acetic Acid

$$NaCH_3COO \rightarrow Na^+ (aq) + CH_3COO^- (aq)$$

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

- Adding *acetate ion* (a product) will shift equilibrium to the **LEFT**
  - ✓ $[H_3O^+]$ will *decrease*
  - ✓ pH will **increase**

Quantitatively

- Example: What happens to the pH when we add 10.00 mL of 0.100 *M* $NaCH_3COO$ to 10.00 mL of 0.100 *M* CH_3COOH?

First: Find intial pH (of the CH_3COOH alone)

	$CH_3COOH (aq) + H_2O (l)$	$\leftrightarrows$ $CH_3COO^- (aq)$	$+ H_3O^+ (aq)$
I	0.100 *M*	0	0
C	-x	+x	+x
E	0.100 - x	x	x

pH of CH_3COOH alone

- Plug into K_a expression:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.76 \times 10^{-5}$$

$$K_a = \frac{(x)(x)}{0.100 - x} = 1.76 \times 10^{-5}$$

- By *successive approximations* (or **quadratic formula)**:

$x = [H_3O^+] = 1.318 \times 10^{-3}\ M$

pH = -Log(1.318×10^{-3}) = ***2.88***

Now, add the $NaCH_3COO$

- We need to re-calculate concentrations when we change the volume of the solution

Trick: use *mmol* instead of **mol**

mL x *M* = *mmol*

10.00 mL x 0.100 *M* CH_3COOH = ***1.00 mmol*** CH_3COOH

10.00 mL x 0.100 *M* $NaCH_3COO$ = ***1.00 mmol*** $NaCH_3COO$

✓Divide by new solution volume to get initial concentrations:

$$\frac{1.00\ \text{mmol}}{20.00\ \text{mL}} = 5.00 \times 10^{-2}\ M$$ (for both CH_3COOH and $NaCH_3COO$)

ICE Time

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

	CH_3COOH	CH_3COO^-	H_3O^+
I	0.0500 *M*	0.0500 *M*	0
C	-x	+x	+x
E	0.0500 - x	0.0500 + x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(0.0500 + x)}{0.0500 - x} = 1.76 \times 10^{-5}$$

Using Successive Approximations: x' = 1.76×10^{-5}

So: $[H_3O^+] = 1.76 \times 10^{-5}\ M$ and pH = ***4.75***

Let's Add Some NaOH

- What would happen to the pH if we added 10.00 mL of 0.0100 *M* NaOH to this soln?

Two possible species to react with OH^-:

$CH_3COO^- + OH^- \rightarrow NR$

Base Base

Is this reaction *quantitative?*

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Acid Base Conj. Base Conj. Acid

What's K?

- Combine two reactions with *known values of K* to get K for the **unknown reaction**:

$$CH_3COOH\ (aq) + H_20\ (l) \rightleftarrows CH_3COO^-\ (aq) + H_3O^+\ (aq) \qquad \boldsymbol{K_a}$$

$$OH^-\ (aq) + H_3O^+\ (aq) \rightleftarrows H_2O\ (l) + H_2O\ (l) \qquad \boldsymbol{1/K_w}$$

$$CH_3COOH\ (aq) + OH^-\ (aq) \rightarrow CH_3COO^-\ (aq) + H_2O\ (l) \qquad \boldsymbol{K}$$

$$\boxed{K = \frac{K_a}{K_w}} = \frac{1.76 \times 10^{-5}}{1.0 \times 10^{-14}} = \underline{\boldsymbol{1.76 \times 10^{9}}}$$

General result for reaction of a weak acid with a strong base

Huge!
Reaction is *quantitative.*

Assume Complete Reaction

- Since K is so large, assume reaction with OH- is *quantitative:*

$$CH_3COOH\ (aq) + OH^-\ (aq) \rightarrow CH_3COO^-\ (aq) + H_2O\ (l)$$

I	1.00 mmol	0.100 mmol	1.00 mmol
C	-0.100 mmol	-0.100 mmol	+0.100 mmol
F	0.90 mmol	0	1.10 mmol

Note: *These are not* ***equilibrium*** *amounts!*

Back to Equilibrium

	$CH_3COOH\ (aq) + H_2O\ (l) \leftrightarrows$	$CH_3COO^-\ (aq)$	$+\ H_3O^+\ (aq)$
I	0.90 mmol/30.00 mL	1.10 mmol/30.00 mL	-
C	-x	+x	+x
E	***3.0 x 10^{-2} -x***	***3.67 x 10^{-2} + x***	***x***

Assume: $x \ll 10^{-2}$

$$\frac{(3.67 \times 10^{-2})x'}{(3.0 \times 10^{-2})} = 1.76 \times 10^{-5}$$

Substituting:

$$1.76 \times 10^{-5} = \frac{(3.67 \times 10^{-2} - x)(x)}{(3.0 \times 10^{-2} + x)}$$

x' = $\boxed{\mathbf{1.44 \times 10^{-5}}\ M = [H_3O^+]}$ (assumption holds: $10^{-5} \ll 10^{-2}$)

Effect on pH?

- ➢pH = $-\text{Log}[H_3O^+]$ = ***4.84***
- ➢So: ΔpH = 4.75 - 4.84 = ***-0.09***

Very little change in pH!

Compare with adding NaOH to water:

Add: 10.00 mL 0.0100 *M* NaOH to *20.00 mL H_2O*

$$[OH^-] = \frac{0.100 \text{ mmol } OH^-}{30.00 \text{ mL}} = \mathbf{3.33 \times 10^{-3}}\ M$$

pOH = *2.48*

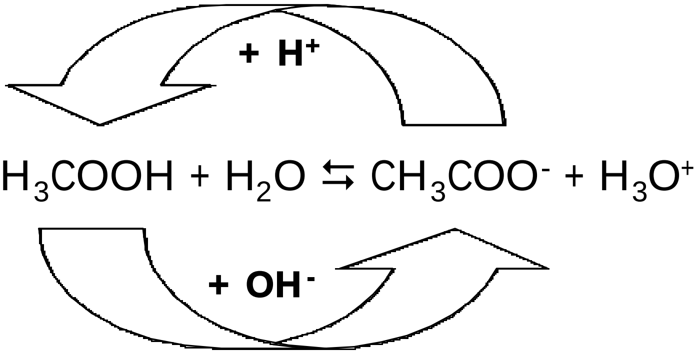
pH = 14.00 - 2.48

pH = ***11.52***

So: ΔpH = 7.00 - 11.52 = ***-4.52*** (Huge!)

Buffers

A mixture of a *weak acid* and its *conjugate base* **buffers** pH:



+ H^+

$$CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$$

+ OH^-

The Henderson-Hasselbalch Equation

- Log formulation of the K_a expression:

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

Solve for $[H_3O^+]$:

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

$$\boxed{\mathbf{pH = pK_a + Log([A^-]/[HA])}}$$

Titrations

- ➢If K_{rxn} is *large*, then it is useful for titrimetric determinations
- ➢We can *predict the pH* of the solution resulting from each addition of titrant in an **acid/base** titration, if we know:
  - ✓Initial concentrations
  - ✓Equilibrium constants

The Process:
-convert to *mmol*
-*complete* reaction
-convert to *concentrations*
-*ICE* to get $[H_3O^+]$
-convert to pH

Example Titration

Let's titrate!

- ➢**Analyte:**
  50.00 mL 0.100 *M* Acetic Acid (HAc)
  $K_a = 1.76 \times 10^{-5}$
- ➢**Titrant:** 0.100 *M* NaOH

The Chemistry:

$HAc + OH^- \rightarrow Ac^- + H_2O$ (titration reaction)

Initial pH (0.00 mL NaOH)

Just HAc (weak acid) alone in solution:

$$HAc + H_2O \leftrightarrows Ac^- + H_3O^+$$

	HAc	Ac^-	H_3O^+
I	0.100 *M*	-	-
C	-x	+x	+x
E	0.100 - x	x	x

$$K_a = \frac{x^2}{0.100 - x}$$

$x = 1.318 \times 10^{-3} = [H_3O^+]$

pH = ***2.88***

5.00 mL NaOH added

Convert to mmol:

- 5.00 mL (0.100 mol OH$^-$/L) = 0.500 mmol OH$^-$
- 50.00 mL (0.100 mol HAc/L) = 5.00 mmol HAc

$$HAc + OH^- \rightarrow Ac^- + H_2O$$

Complete reaction:

	HAc	OH^-	Ac^-
I	5.00 mmol	0.500 mmol	-
C	-0.50 mmol	-0.500 mmol	+0.500 mmol
F	*4.50 mmol*	-	*0.500 mmol*

Convert to concentrations:

$$C_{HAc} = \frac{4.50\ mmol}{55.00\ mL} = \underline{8.182 \times 10^{-2}\ M}$$

$$C_{Ac^-} = \frac{0.50\ mmol}{55.00\ mL} = \underline{9.091 \times 10^{-3}\ M}$$

It's a Buffer!

On to Equilibrium!

$$HAc + H_2O \leftrightarrows Ac^- + H_3O^+$$

I	8.182 x 10^{-2} *M*	9.091 x 10^{-3} *M*	-
C	-x	+x	+x
E	*8.182 x 10^{-2} - x*	*9.091 x 10^{-3} + x*	*x*

pH = pK_a + Log([Ac^-]/[HAc])

pH = 4.754 + Log [(*9.091 x 10^{-3} + x*)/(*8.182 x 10^{-2} - x*)]

<u>Assume:</u> x << 10^{-2}

pH = 4.754 + Log(*9.091 x 10^{-3}/8.182 x 10^{-2}*) = 3.7998 = ***<u>3.80</u>***

25.00 mL NaOH added

It's a Buffer!

Convert to mmol:

- 25.00 mL (0.100 mol OH^-/L) = 2.50 mmol OH^-
- 50.00 mL (0.100 mol HAc/L) = 5.00 mmol HAc

$$HAc + OH^- \rightarrow Ac^- + H_2O$$

Complete reaction:

I	5.00 mmol	2.50 mmol	-
C	- 2.50 mmol	- 2.50 mmol	+2.50 mmol
F	*2.50 mmol*	-	*2.50 mmol*

pH = pK_a + Log([Ac^-]/[HAc])

pH = pK_a + Log(1) = 4.754 + 0 = ***<u>4.75</u>***

What are we assuming when we do this?

50.00 mL NaOH added

Equiv. Point

Convert to mmol:

- 50.00 mL (0.100 mol OH^-/L) = 5.00 mmol OH^-
- 50.00 mL (0.100 mol HAc/L) = 5.00 mmol HAc

$$HAc + OH^- \rightarrow Ac^- + H_2O$$

Complete reaction:

	HAc	OH^-	Ac^-	H_2O
I	5.00 mmol	5.00 mmol	-	
C	- 5.00 mmol	-5.00 mmol	+5.00 mmol	
F	-	-	*5.00 mmol*	

Convert to concentrations:

$$C_{Ac^-} = \frac{5.00\ \text{mmol}}{100.00\ \text{mL}} = \underline{5.00 \times 10^{-2}\ M}$$

Equilibrium: Weak Base

$$Ac^- + H_2O \leftrightarrows HAc + OH^-$$

	Ac^-	H_2O	HAc	OH^-
I	$5.00 \times 10^{-2}\ M$		-	-
C	-x		+x	+x
E	$5.00 \times 10^{-2}\ M - x$		x	*x*

$K_b = K_a/K_w = 5.68 \times 10^{-10}$

$$K_b = \frac{x^2}{0.0500 - x}$$

$x = 5.33 \times 10^{-6} = [OH^-]$

pOH = *5.27*

pH = 14.00 - *5.27* = $\boxed{\underline{\mathbf{8.73}}}$

60.00 mL NaOH added

Convert to mmol:

- 60.00 mL (0.100 mol OH^-/L) = 6.00 mmol OH^-
- 50.00 mL (0.100 mol HAc/L) = 5.00 mmol HAc

$$HAc + OH^- \rightarrow Ac^- + H_2O$$

Complete reaction:

	HAc	OH^-	Ac^-
I	5.00 mmol	6.00 mmol	-
C	- 5.00 mmol	-5.00 mmol	+5.00 mmol
F	-	*1.00 mmol*	*5.00 mmol*

Two bases - which one will control pH?

Excess OH^- Rules!

$$[OH^-] = [OH^-]_{NaOH} + [OH^-]_{Ac-} + [OH^-]_{H2O}$$

$$[OH^-] = \frac{1.00\text{ mmol}}{110.00\text{ mL}} + (<10^{-6}) + (<10^{-7})$$

$$[OH^-] = 9.091 \times 10^{-3}\ M$$

pOH = ***2.04***

pH = 14.00 - *2.04* = ***11.96***

Equivalence Point Detection

- *Inflection Point* of titration curve
  - Plot *pH versus mLs titrant*
- Indicator

$$\underset{\text{acid form}}{HIn} \leftrightarrows H^+ + \underset{\text{base form}}{In^-}$$

- Color change observed when: $[HIn] = [In^-]$
  (when $pH = pK_a$ of indicator)
- Choose indicator so that:
  Indicator pK_a » *Equiv Pt pH*

Polyprotic Acids

- What if an acid has more than one acidic proton?

Example: H_2CO_3

$H_2CO_3 \leftrightarrows H^+ + HCO_3^-$ $K_1 = 4.3 \times 10^{-7}$

$HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$ $K_2 = 4.8 \times 10^{-11}$

If K_1 >> **K_2:** Treat as *separate acids*

Titration of H_2CO_3

Reaction with OH^- occurs *stepwise:*

H_2CO_3 reacts first:

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$

HCO_3^- reacts only once all H_2CO_3 is gone:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

H_2CO_3: Weak Acid	H_2CO_3/HCO_3^-: Buffer
CO_3^{2-}: Weak Base	HCO_3^-/CO_3^{2-} : Buffer

HCO_3^-: *Amphoteric* (acts as both acid and a base)

Dealing with HCO_3^-

- **Will a solution of HCO_3^- be acidic or basic?**

Two equilibria:

$HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$ $K_2 = 4.8 \times 10^{-11}$

$HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^-$ $K_b = K_w/K_1 = 2.3 \times 10^{-8}$

$K_b > K_2$, so HCO_3^- is a stronger *base* than acid
(solution will be basic)

Quantitatively?

- It can be shown that:

$$[H^+] = \left[\frac{K_1K_2[HA^-] + K_1K_w}{K_1 + [HA^-]}\right]^{1/2}$$

✓<u>But</u> HCO_3^- is such a weak acid/base that it dissociates very little: $[HCO_3^-] \approx C_{HCO3-}$

✓Also, if: $C_{HCO3-} >> K_1$ and $K_2 >> K_w$

<u>THEN:</u> $\boxed{[H^+] = (K_1K_2)^{½}}$ ($pH = ½[pK_1 + pK_2]$)