Name	Formula	K,	pK,
Hydroiodic acid	HI	large ~10 ¹¹	-11
Perchloric acid	HClO ₄	large ~10 ¹⁰	-10
Hydrobromic acid	HBr	large ~10 ⁹	-9
Hydrochloric acid	HCL	large ~10'	-7
Chloric acid	HClO ₃	large ~10 ³	-3
Sulfuric acid	H ₂ SO ₄	large ~10 ²	-2
Nitric acid	HNO ₃	large ~10	-1
Hydronium ion	H ₃ 0 ⁺	1.0	0
Trichloroacetic acid	CCl ₃ CO ₂ H	3.0×10^{-1}	0.52
Iodic acid	HIO ₃	1.6×10^{-1}	0.80
Sulfurous acid	H ₂ SO ₃	$1.5 imes 10^{-2}$	1.82
Hydrogen sulfate	HS07	1.2×10^{-2}	1.92
Chlorous acid	HClO ₂	1.1×10^{-2}	1.96
Phosphoric acid	H ₃ PO ₄	7.5×10^{-3}	2.12
Hydrofluoric acid	HF	6.8×10^{-4}	3.17
Nitrous acid	HNO ₂	4.5×10^{-4}	3.35
Formic acid	HCO ₂ H	1.8×10^{-4}	3.74
Benzoic acid	C ₆ H ₅ CO ₂ H	6.3×10^{-5}	4.20
Acetic acid	CH ₃ CO ₂ H	1.8×10^{-5}	4.74
Propionic acid	CH ³ CH ³ CO ³ H	1.3×10^{-5}	4.89
Carbonic acid	H ₂ CO ₃	4.3×10^{-7}	6.37
Hydrogen sulfite	HS05	1.2×10^{-7}	6.91
Dihydrogen phosphate	H ₂ PO ₄	6.2×10^{-8}	7.21
Hypochlorous acid	HCLO	3.0×10^{-8}	7.52
Hypobromous acid	HBrO	2.3×10^{-9}	8.64
Ammonium ion	NH	5.6×10^{-10}	9.26
Hydrocyanic acid	HCN	4.0×10^{-10}	9.40
Phenol	C _s H _s OH	1.6×10^{-10}	9.80
Hydrogen carbonate	HC05	5.6×10^{-11}	10.25
Hypoiodous acid	HIO	2.3×10^{-11}	10.64
Hydrogen phosphate	HPO ₄ ²⁻	3.6×10^{-13}	12.44

Metal Ion	Ka	pK,
$[Fe(H_2O)_6]^{3+}$	$3.5 imes 10^{-3}$	2.46
$[Cr(H_20)_6]^{3+}$	$1.3 imes 10^{-4}$	3.89
$[Al(H_20)_6]^{3+}$	$7.9 imes 10^{-6}$	5.10
[Cu(H ₂ 0) ₆] ²⁺	$3.2 imes 10^{-8}$	7.49
[Co(H ₂ 0) ₆] ²⁺	1.3×10^{-9}	8.89
$[Ni(H_20)_6]^{2+}$	2.5×10^{-11}	10.6
$[Mg(H_20)_6]^{2+}$	zero	
$[Na(H_20)_6]^+$	zero	

- Today we have two goals:
 - Calculating the pH of complex salt solutions
 - Polyprotic acids
- The big picture:
 - All these aqueous acid/base problems are examples of simultaneous equilibrium.
 - This general situation is very common in chemical engineering.
 - Batch fed reactions and fermentations
- We'll be looking at some acid/base examples, but all the concepts are the same.

• In the first example we have to worry about the anion:

$$NaCN(s) \longrightarrow Na^{+}(aq) + CN^{-}(aq)$$

Na⁺: Group 1A metal, just solvates CN⁻: Anion of a weak acid. Will equilibrate in water. HCN K_a = 4 x 10⁻¹⁰

It is imperative to understand the species you have in solution. It's why we memorized all those ions and the strong acids!

 Example: What is the pH of a 1 M solution of NaCN?

$$CN^{-}(aq) + H_2O \xrightarrow{K_b} HCN(aq) + OH^{-}(aq)$$

Equil: 1 - x x x

$$CN^{-}(aq) + H_2O \xrightarrow{K_b} HCN(aq) + OH^{-}(aq)$$

Equil: 1 - x x x
$$K_b = \frac{(x)(x)}{1.0 - (x)}$$

$$K_{w} = K_{a}K_{b}$$

$$K_{b} = \frac{K_{w}}{K_{a}} = \frac{1x10^{-14}}{4x10^{-10}} = 2.5x10^{-5}$$

$$2.5x10^{-5} = \frac{(x)(x)}{1.0 - (x)} = x^{2} \text{ (x has to be much smaller than 1.0)}$$

$$5x10^{-3} = x$$

$$[OH^{-}] = 5x10^{-3}$$

$$pOH = -\log(5x10^{-3}) = 2.3$$

$$pH = 14 - pOH = 14 - 2.3 = 11.7$$

- Now we'll look at a more complicated situation: when both the anion and the cation are the salts of a weak acid/base.
- Example what is the pH of a 0.2 M solution of NH₄F? NH₄⁺ is a weak acid, F⁻ is the conjugate base of a weak acid.

•
$$NH_4F(aq) \implies NH_4^+(aq) + F^-(aq)$$

• Salt weak acid weak base

Example: What is the pH of a 0.2 M solution of NH_4F ? NH_4^+ is a weak acid, F^- is the conjugate base of a weak acid (which is a weak base).

$$NH_4F \longrightarrow NH_4(aq) + F^-(aq)$$

 $NH_4^+(aq) + H_2O \implies NH_3(aq) + H_3O^+(aq)$ $K_a = 5.6 \times 10^{-10}$ $F^-(aq) + H_2O \implies HF(aq) + OH^-(aq)$ $K_b = 1.47 \times 10^{-11}$

Example: What is the pH of a 0.2 M solution of NH_4F ? NH_4^+ is a weak acid, F^- is the conjugate base of a weak acid.

$$\begin{aligned} \text{NH}_4^+(\text{aq}) + \text{H}_2 & \longrightarrow \text{NH}_3(\text{aq}) + \text{H}_3 O^+(\text{aq}) & \text{K}_a = 5.6 \text{x} 10^{-10} \\ \text{F}^-(\text{aq}) + \text{H}_2 O & \longrightarrow \text{HF}(\text{aq}) + \text{OH}^-(\text{aq}) & \text{K}_b = 1.47 \text{x} 10^{-11} \\ \text{H}_3 O^+ + \text{OH}^- & \longrightarrow 2 \text{H}_2 O & 1/\text{K}_w = 1 \text{x} 10^{-14} \end{aligned}$$

Net: $NH_4^+(aq) + F^- \longrightarrow NH_3 + HF$



Example: What is the pH of a 0.2 M solution of NH_4F ? NH_4^+ is a weak acid, F^- is the conjugate base of a weak acid.

$$\begin{aligned} NH_4^+(aq) + H_2O &= NH_3(aq) + H_3O^+(aq) & K_a = 5.6 \times 10^{-10} \\ F^-(aq) + H_2O &= HF(aq) + OH^-(aq) & K_b = 1.47 \times 10^{-11} \\ H_3O^+ + OH^- &= 2H_2O & 1/K_w = 1 \times 10^{-14} \end{aligned}$$

Net: $NH_4^+(aq) + F^- \longrightarrow NH_3 + HF$

$$K = \frac{K_a^{(NH_4^+)} K_b^{F^-}}{K_w}$$

Now we're gonna get into acids that can give up more than one proton.

Do you think that both H's will dissociate as easily, or do you think they'll be different?

Why?

The strongest polyprotic acid is sulfuric acid:

 $H_2SO_4 \implies HSO_4^- + H_3O^+ \quad K_{a1} > 1$ $HSO_4^- \implies SO_4^{2-} + H_3O^+ \quad K_{a1} > 1.2x10^{-2}$

The pH of sulfuric acid solution will depend on both equilibria. The math is simpler because the first dissociation is complete.

Another example, phosphoric acid (H_3PO_4) :

 $H_{3}PO_{4} = H_{2}PO_{4}^{-} + H_{3}O^{+}$ $H_{2}PO_{4}^{-} = HPO_{4}^{2-} + H_{3}O^{+}$ $HPO_{4}^{2-} = PO_{4}^{3-} + H_{3}O^{+}$ $K_{a3}=3.6x10^{-11}$

The 10^5 reduction in K_{a2} versus K_{a1} means that the second dissociation will have a negligible effect on the pH of the solution.

Unfortunately, for you, the pH of sulfuric acid depends on both dissociations, so let's do that problem!

Example, what is the pH of a 0.1 M solution of H_2SO_4 ?

H_2SO_4	$HSO_4^- +$	H_3O^+	K _{a1} big
0.1 M	0	0	
0	0.1	0.1	
HSO_4^{2-}	$= SO_4^{2-} +$	- H ₃ O ⁺	$K_{a1} = 1.2 \times 10^{-2}$
0.1	0	0.1	
$0.1_{-}v$	v	0 1 ⊥ v	
	$H_{2}SO_{4}$ $0.1 M$ 0 $HSO_{4}^{2-} = 0.1$ $0.1 - x$	$H_{2}SO_{4} HSO_{4}^{-} + 0.1 M 0 0 0.1$ $HSO_{4}^{2-} = SO_{4}^{2-} + 0.1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0$	$H_{2}SO_{4} HSO_{4}^{-} + H_{3}O^{+}$ $0.1 M 0 0$ $0 0.1 0.1$ $HSO_{4}^{2-} \longrightarrow SO_{4}^{2-} + H_{3}O^{+}$ $0.1 0 0.1$

Diprotic acids

Example, what is the pH of a 0.1 M solution of H_2SO_4 ?

	H_2SO_4	HSO_4^- -	H_3O^+	K _{a1} big
start:	0.1 M	0	0	
end:	0	0.1	0.1	
	HSO_4^{2-}	$rac{}{}$ SO ₄ ²⁻	+ H ₃ O ⁺	$K_{a1} = 1.2 \times 10^{-2}$
start:	0.1	0	0.1	
end	0.1-x	Х	0.1+x	
$1.2x10^{-2} = -$	$\frac{\left[SO_4^{2-}\right]\left[H_3O^+\right]}{\left[HSO_4^-\right]} = 0$	$\frac{(x)(.1+x)}{.1-x}$		
$1.2x10^{-2}(1-$	$-x) = .1x + x^2$			
$0 = x^2 + 0.1$	12x - 0.0012			
Use the qua	adratic equation:			
$x = \frac{-0.112}{-0.112}$	$\pm \sqrt{(.112)^2 - 4(1)(.22)^2}$	-0.0012) =	0.01 So at	equilibrium:
$[SO_4^{2-}] = 0.0$	01 <i>M</i>			
$\left[H_3O^+\right] = 0$.1 + x = 0.11M			
$\left[HSO_4^{-}\right] = 0$	0.1 - x = 0.09M			
$pH = -\log(pH)$	(0.11) = 0.96			
Percent ful	ly ionized: $=\frac{[Solution]{[H_2]}}{[H_2]}$	$\frac{O_4^{2-}]}{SO_4} x100\%$	$\delta = \frac{0.01M}{0.10M}$	-x100% = 10%

More polyprotic acids

- Today we have two goals:
 - More polyprotic acids: phosphoric acid and its salts
 - Neutralization reactions
- The big picture:

Why Phosphate? Phosphate is one of the most important buffer systems inside cells.

• We'll be looking at some acid/base examples

More polyprotic acids

Last Time we talked about a strong polyprotic acid, sulfuric acid. In this case the K_a 's are close to each other (>1 and 10⁻²).

However, for weak polyprotic acids, like phosphoric acid or carbonic acid, this is not the case. The K_a 's are quite far from each other.

We're gonna use phophoric acid as our example:

Phosphoric acid equilibrium phosphoric acid (H₃PO₄):

 $H_{3}PO_{4} = H_{2}PO_{4}^{-} + H_{3}O^{+} \qquad K_{a1} = 7.5 \times 10^{-3}$ $H_{2}PO_{4}^{-} = HPO_{4}^{-2-} + H_{3}O^{+} \qquad K_{a2} = 6.2 \times 10^{-8}$ $HPO_{4}^{-2-} \qquad PO_{4}^{-3-} + H_{3}O^{+} \qquad K_{a3} = 3.6 \times 10^{-11}$

The 10^5 reduction in K_{a2} versus K_{a1} means that the second dissociation will have a negligible effect on the pH of the solution.

Phosphoric acid equilibrium Example: What is the pH of 0.1M H_3PO_4 ? $H_3PO_4 = H_2PO_4 + H_3O^+ = K_{a1} = 7.5 \times 10^{-3}$ 0.1 0 ()0.1-x X X $K_{a1} = 7.5x10^{-3} = \frac{\left[H_2 P O_4^{-}\right]\left[H_3 O^{+}\right]}{\left[H_3 P O_4^{-}\right]} = \frac{(x)(x)}{.1 - x}$ $7.5x10^{-4} = x^2$

0.027M = x

Oops! This number is too close to .1 to ignore it in denominator:

 $\frac{(0.027)^2}{(1-0.027)^2} \approx 10x10^{-4} \text{ So let's just guess some numbers. Must be smaller:}$ $\frac{(0.023)^2}{(1-0.023)^2} \approx 6.9x10^{-4}$ $\frac{(0.024)^2}{(1-0.024)^2} \approx 7.6x10^{-4}$ $pH = -\log(0.024) = 1.62$

Phosphoric acid equilibrium What is the pH of 0.1M NaH₂PO₄? H₂PO₄⁻ \longrightarrow HPO₄²⁻ + H₃O⁺ K_{a2}=6.2x10⁻⁸ H₂PO₄⁻ + H₂O \longrightarrow H₃PO₄ + OH⁻ K_b=K_w/K_{a1}=1x10⁻¹⁴/7.5x10⁻³=1.3x10⁻¹²

It's exactly like $NH_4F(s)$. We have three equilibria, the two above plus water.

 $H_{2}PO_{4}^{-} \implies HPO_{4}^{2-} + H_{3}O^{+} \qquad K_{a2} = 6.2 \times 10^{-8}$ $H_{2}PO_{4}^{-} + H_{2}O \implies H_{3}PO_{4} + OH \qquad K_{b1} = 1.3 \times 10^{-12}$ $H_{3}O^{+} + OH \implies 2H_{2}O \qquad K_{w} = 1 \times 10^{-14}$ $2H_{2}PO_{4}^{-} \implies HPO_{4}^{2-} + H_{3}PO_{4} \qquad K = \frac{(K_{a2})(K_{b1})}{K_{w}}$

$$pH = \frac{1}{2}(pK_a^{(H_2PO_4^-)} + pK_a^{(H_3PO_4)}) = \frac{1}{2}\{(-\log(6.2x10^{-8}) + -\log(7.5x10^{-3}))\} = 4.66$$

Phosphoric acid equilibrium

So, *in general,* for an intermediate salt of a polyprotic acid:

 $\begin{array}{rcl} HA^- + H_2O_{(1)} & & H_3O^+ + A^{2-} K_{a2} \\ HA^- + H_2O_{(1)} & & H_2A + OH^- & K_{b1} = K_w/K_{a1} \\ pH &= 1/2\{pKa_2 + pKa_1\} & pH \text{ is independent of concentration} \\ pH \text{ is average of } pKa's \text{ for the} \\ anion \text{ and its conjugate acid.} \\ \end{array}$

Generally:
$$MX(s) = M^+(aq) + X^-(aq)$$

 $1 > K_a > 10^{-14} + 1 > K_b > 10^{-14}$

then: $pH = 1/2\{pKa_2 + pKa_1\}$

To summarize for phosphoric acid H₃PO₄

- 1. H_3PO_4 : H_3O^+ will come from K_{a1} , the first ionization reaction
- 2. $H_2PO_4^-$: amphiprotic; $pH = 1/2\{pK_{a1} + pK_{a2}\}$
- 3. HPO_4^{2-} : amphiprotic, $pH = 1/2\{pK_{a2} + pK_{a3}\}$
- 4. PO_4^{3-} : by hydrolysis of water; $k_b = K_w/K_{a3} = 2.8 \times 10^{-4}$

Neutralization -

Acids and bases react in a process called *neutralization*.

1. Add a strong acid to a weak base, NH₃

Acid: HCl(aq) + H₂O(l) \longrightarrow H₃O⁺(aq) + Cl⁻(aq) K_a >> 1

Base:
$$NH_3(aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$$
 $K_b = 1.8 \times 10^{-5}$
 $H_3O^+ + OH^- \longrightarrow 2H_2O(l)$ $K = 1/K_w$

Net: $NH_3(aq) + H_3O^+(aq) \longrightarrow NH_4^+(aq) + OH^-(aq) K = K_{b'}(1/K_w)$

2. Weak acid + weak base, example:

 $\begin{array}{c} CH_{3}CO_{2}H + NH_{3} \\ CH_{3}CO_{2}H + H_{2}O(1) &\longrightarrow CH_{3}CO_{2}^{-} + H_{3}O^{+}(aq) & K_{a} = 1.8 \times 10^{-5} \\ NH_{3}(aq) + H_{2}O(1) &\longrightarrow NH_{4}^{+}(aq) + OH^{-}(aq) & K_{b} = 1.8 \times 10^{-5} \\ H_{3}O^{+} + OH^{-} &\longrightarrow 2H_{2}O(1) & K = 1/K_{w} \end{array}$

Net: $CH_3CO_2H + NH_3(aq) \longrightarrow CH_3CO_2^- + NH_4^+ = K_aK_b\left(\frac{1}{K_w}\right) = \left(\frac{(1.8x10^{-5})(1.8x10^{-5})}{1x10^{-14}}\right) = 3.2x10^4$

Goes to completion.

Neutralization -

For any neutralization reaction:

- 1. strong acid weak base $K = K_b/K_w$
- 2. Strong base weak acid $K = K_a/K_w$
- 3. Weak acid weak base $K = K_a K_b / K_w$ All that are >1 go to completion.

Neutralization reactions are used in titration to evaluate the concentrations and strengths of acids and bases.

Neutralization – Example problem:

- Problem: 20 mL of 1.0 M HCl are added to 1L of 0.1 M $NH_3(aq)$ in water. What are the concentrations of [OH⁻], [NH₃] and [NH₄⁺] at equilibrium?
- There are two processes occuring:
- I. Neutralizaton

 $NH_3 + HCI NH_4^+ + CI^-$ St 0.1M(1L) 0.02L(1M) 0 0 0.1 mole 0.02 moles

End: 0.1-.02=.08mol 0 0.08mole/1.02L=0.078M 0.02mol .02mol .02mol/1.02=0196M

Neutralization

 II. The equilibrium between ammonia & ammonium:

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

 St. 0.078M
 0.0196M
 0M

 End: 0.078-x
 0.0196+x
 x

 $1.8x10^{-5} = \frac{[[NH]]_{4}^{+}][OH^{-}]}{[NH_{3}]} = \frac{(0.0196 + x)(x)}{0.078 - x}$ You can safely ignore the x's and rearrange: $x = \frac{(1.8x10^{-5})(0.078)}{0.0196} = 7.16x10^{-5}$

[NH₃]=0.078M [NH₄⁺]=0.0197M

This is probably the most important part of the section.

We will cover:

- 1. The common ion effect
- 2. Buffered solutions
- 3. Buffering capacity
- 4. The Henderson-Hassellbach equation
- 5. Preparing a buffer.

Buffering is all about controlling pH. Even if the concentrations are small, large changes in pH can have huge effects on chemical reactions.

In biology, this is particularly critical as the intracellular pH of virtually all cells in nature is around neutral, and significant deviations have profound effects on function.

We'll learn here how to keep pH steady.

We'll start with an example that shows how buffering works:

Example: What is the pH of a solution of 0.1M acetic acid (CH₃COH) and 0.1M sodium acetate $(NaCH_3CO_2^{-})$?

Start with equilibrium of acetic acid/acetate:

 $CH_{3}CO_{2}H + H_{2}O(1) = CH_{3}CO_{2} + H_{3}O^{+}(aq) K_{a} = 1.8 \times 10^{-5}$ Init: 0.1 mole 0.1 mole 0 final: 0.1-x 0.1+x x

$$K_a = 1.8x10^{-5} = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(0.1+x)(x)}{(0.1-x)}$$

Will x be small? What are you comparing it to?

Example problem: consisting of 0.1M acetic acid (CH₃COH) and 0.1M sodium acetate (NaCH₃CO₂⁻)

$$CH_{3}CO_{2}H + H_{2}O(1) - CH_{3}CO_{2} + H_{3}O^{+}(aq) K_{a} = 1.8 \times 10^{-5}$$

Init: 0.1 mole 0
final: 0.1-x 0.1+x x

$$K_{a} = 1.8 \times 10^{-5} = \frac{[CH_{3}CO_{2}^{-}][H_{3}O^{+}]}{[CH_{3}CO_{2}H]} = \frac{(0.1 + x)(x)}{(0.1 - x)}$$

Will x be small? What are you comparing it to? **1.8x10⁻⁵ is a lot smaller than 0.1, so x has to be small compared to 0.1.**

$$1.8x10^{-5} = \frac{0.1(x)}{0.1} = x \colon pH = -\log(1.8x10^{-5}) = 4.74$$

 $CH_{3}CO_{2}H + H_{2}O(1) = CH_{3}CO_{2} + H_{3}O^{+}(aq) K_{a} = 1.8 \times 10^{-5}$ Common ion effect

Manifestation of LeChatlier's principle

Common ion effect: Adding a reagent that contains an ion already at equilibrium in solution will push the equilibrium the other direction.

Here, adding H_3O^+ pushes the equilibirum to left, absorbing acid.

If both acetate and acetic acid are added to a solution, changes in pH will be resisted in *both directions*. Added acid will be absorbed by acetate. Added base will be absorbed by acetic acid.

Example: What is the pH of the solution after addition of 10 mL of 1M HCI (to 1L)?

 $CH_{3}CO_{2}H + H_{2}O(1) - CH_{3}CO_{2} + H_{3}O^{+}(aq) K_{a}=1.8 \times 10^{-5}$ Init: 0.1 mole 0.1 mole 1.8 \times 10^{-5} mole change: 0.1+.01=0.11 mole 0.1-.01=.09 equilib: .11/1.01L-x 0.09/1.01L+x x $1.8 \times 10^{-5} = \frac{[CH_{3}CO_{2}^{-}][H_{3}O^{+}]}{[CH_{3}CO_{2}H]} = \frac{(0.09/1.01L + x)(x)}{(0.11/1.01L - x)} = \frac{.09x}{.11}$ $x = \frac{.11}{.09}(1.8 \times 10^{-5}) = 2.2 \times 10^{-5}$ $pH = -\log(2.2 \times 10^{-5}) = 4.66$

Lets compare the result of adding 10 mL of 1M HCl to 1L *without* the buffer:

$$[H_3O^+] = \frac{0.01L(1MH_3O^+)}{1.01L} = 9.9 \times 10^{-3} \text{ pH} = -\log(9.9 \times 10^{-3}) = 2.00$$

$$1.8x10^{-5} = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(0.09/1.01L + x)(x)}{(0.11/1.01L - x)} = \frac{.09x}{.11}$$
$$x = \frac{.11}{.09}(1.8x10^{-5}) = 2.2x10^{-5}$$
$$pH = -\log(2.2x10^{-5}) = 4.66$$

Lets compare the result of adding 10 mL of 1M HCl to 1L *without* the buffer:

$$[H_3O^+] = \frac{0.01L(1MH_3O^+)}{1.01L} = 9.9x10^{-3} \text{ pH} = -\log(9.9x10^{-3}) = 2.00$$

Buffer:

No Buffer:



Now, let's go the opposite way and see what happens when we add base, for example 20 mL of 1M NaOH.

NaOH
$$\longrightarrow$$
 Na⁺ + OH⁻ Full dissociation.
.02-.02 .02 .02
OH⁻ + CH₃CO₂H \longrightarrow CH₃CO₂⁻ + H₂O(aq)
st. .02mol .1mol . 1mol
eq. 0 .1-.02=.08 mol .1+.02=0.12mol

 $CH_{3}CO_{2}H + H_{2}O(1) = CH_{3}CO_{2} + H_{3}O^{+}(aq) K_{a} = 1.8 \times 10^{-5}$ Init: .08 mole 0.12 mole change: -x +x +x equilib: .08/1.02 - x .12/1.02 + x x

Now, let's go the opposite way and see what happens when we add base, for example 20 mL of 1M NaOH.

CH	$H_3CO_2H + H_2O(1)$	$CH_3CO_2 + H$	$I_{3}O^{+}(aq)$	$K_a = 1.8 \times 10^{-5}$
Init:	.08 mole	0.12 mole		
change:	-X	+X	+X	
equilib:	.08/1.02-x	.12/1.02+x	Х	

$$1.8x10^{-5} = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(0.12/1.02L + x)(x)}{(0.08/1.02L - x)} = \frac{.12x}{.08}$$
$$x = \frac{.08}{.12}(1.8x10^{-5}) = 1.2x10^{-5}$$
$$pH = -\log(1.2x10^{-5}) = 4.92$$

Note, in both of these cases where the buffer is working, there is still plenty of both acetate and acetic acid. If one runs out, the buffer will not work anymore. If acetate runs out, there is only acetic acid and only base can be buffered. If acid runs out, only acid can be buffered.

The Henderson Hasselbach equation

All this can be summarized with a very convenient equation, *the Henderson Hasselbach equation.* It is a favorite tool of biochemists.

 $HA + H_2O \implies A^- + H_3O^+(aq)$ $K_a = \frac{[A^-][H_3O^+]}{[HA]}$ $-\log K_a = -\log[H_3O^+] - \log\left\{\frac{\lfloor A^-\rfloor}{\lfloor HA\rfloor}\right\}$ $pK_a = pH - \log\left\{\frac{[A^-]}{[HA]}\right\}$ $pH = pK_a + \log\left\{\frac{[A^-]}{[HA]}\right\}$ The pH of any buffer can be known with the pK_a of weak acid & concentrations of HA and A⁻ the pH of Centered a buffer It can be varied by +/- 1 pH unit by on pK_a of system is changing A-/HA ratio from 0.1 to 10. weak acid More than that, one of them will be too low in concentration.

The blood carbonate buffer system

Example: Carbonic acid, H_2CO_3 , and it's conjugate base, HCO₃⁻, are responsible for maintaining the pH of blood at 7.40. Calculate the ratio of the two conjugate partners necessary to establish a buffer of pH = 7.4.

 $H_2CO_3 + H_2O = HCO_3^- + H_3O^+(aq) K_a = 8.0 \times 10^{-7} \text{ at } 37^{\circ}C$ $pH = pK_a + \log\left\{\frac{\lfloor A^- \rfloor}{\lfloor HA \rfloor}\right\}$ $pH = pK_a + \log\left\{\frac{[HCO_3^-]}{[H_2CO_3]}\right\}$ $7.4 = -\log(8.0x10^{-7}) + \log\left\{\frac{[HCO_3^-]}{[H_2CO_3]}\right\}$ $7.4 = 6.10 + \log \left\{ \frac{[HCO_3^-]}{[H_2CO_3]} \right\}$ $1.3 = \log \left\{ \frac{[HCO_3^-]}{[H_2CO_3]} \right\}$ In blood, the arterial concentrations are: [HCO_3^-]=0.024M $[H_2CO_3]=0.0012M$ $10^{1.3} = \frac{[HCO_3^-]}{[H,CO_3]} = 20$

Buffer Design

Design a buffer system for a pH of 7.5. Let's use phosphate. For a pH of 7.5, we need a pKa in the right range: $H_2PO_4^- + H_2O = HPO_4^{2-} + H_3O^+(aq) K_a = 6.2x10^{-8}$ $-\log(6.2 \times 10^{-8}) = 7.27$, so close to 7.5. $pH = pK_a + \log\left\{\frac{[A^-]}{[HA]}\right\}$ $pH = pK_a + \log\left\{\frac{[HPO_4^{2^-}]}{[H_2PO_4^{-}]}\right\}$ $7.5 = -\log(6.2x10^{-8}) + \log\left\{\frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]}\right\}$ $7.5 = 7.21 + \log\left\{\frac{[HPO_4^{2^-}]}{[H_2PO_4^-]}\right\}$ *Note*: When the concentrations of $HA = A^{-1}$: $0.29 = \log \left\{ \frac{[HPO_4^{2^-}]}{[H_2PO_4^{-}]} \right\}$ $pH = pKa + \log \frac{[A^-]}{[HA]} = pKa + \log 1 = pKa$ The pH = pKa $10^{0.29} = \frac{[HPO_4^{2^-}]}{[H PO_4^{-1}]} = 1.96$

A 2:1 molar ratio of Na₂HPO₄:NaH₂PO₄ will give you a pH=7.5.