Slide 1	Chemical Equilibrium Acids & Bases in Aqueous Solution	
Slide 2	K is K is K is K No matter what type of reaction you are talking about – equilibrium properties remain the same. K _c , K _p , K _a , K _b , K _w , K _{sp} , K _f The subscripts refer to certain specific TYPES of equilibria, but	
Slide 3	K is K is K	

Slide 4	What is an acid? Bronsted-Lowry definition: An acid is a proton donor. So, what's a base? Bronsted-Lowry definition: A base is a proton acceptor.	
Slide 5	They go togetherlike carrots and peas,	
	Forrest. If you are going to donate a proton, something must accept it.	
	You can't really be an acid without a base.	
Slide 6	What's the most common acid? Water!!	
	H-OH, it has a proton it can donate.	

Slide 7	What's the most common base? Water! "" H - O - H "" It has extra electrons on the oxygen, so a proton can stick to it.			
Slide 8	Water is special it is amphoteric: it can act as an acid or a base. It's not the only compound that can, we'll see other's later. It also means that most Bronsted-Lowry acids or bases can dissolve in water.	-		
Slide 9	We like water Acids and bases like water So, acids and bases are mostly found as aqueous solutions here. Like all solutions, the concentration is a critical parameter.	- - - -		

Slide 10	All solutions are created equal Like any other aqueous solution, a solution of either an acid or base is defined by its concentration. So what's this thing called pH?	
Slide 11	pH is concentration The pH scale is just a logarithmic scale for the Molarity of the protons in the solution. The pH scale is logarithmic (the difference between pH=1 and pH=2 is a factor of 10) pH is concentration	
Slide 12	Damn those logs pH = - log [H+] [x] always means "concentration of x" [H+] should be in M. pH is ONLY the concentration of H+-	

Example

0.1 M HCl solution. What's the pH? $Implicitly, \ you \ must \ recognize \ that: \\ HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

$$\label{eq:continuous} \text{Or,} \qquad \text{HCl}_{(\text{aq})} \, + \, \text{H}_2 \text{O}_{(\text{I})} \rightarrow \text{H}_3 \text{O}^+_{(\text{aq})} + \, \text{Cl}^-_{(\text{aq})}$$

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Slide 14

What is pH?

 $pH = - log [H_3O^+] = - log [H^+]$

 $\rm H_3O^+$ is just an $\rm H^+ + \rm H_2O$

Protons don't float around freely in water, they ALWAYS hook up with a water molecule.

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Slide 15

Example

0.1 M HCl solution. What's the pH? $Implicitly, you must recognize that: \\ HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

$$\mbox{Or,} \qquad \mbox{HCl}_{(aq)} \, + \, \mbox{H}_2\mbox{O}_{(l)} \rightarrow \mbox{H}_3\mbox{O}^+_{(aq)} + \, \mbox{Cl}^-_{(aq)}$$

 $pH = - log [H^+] = - log [H_3O^+]$ pH = - log (0.1 M) = 1.0

,			

Slide 16

We made an assumption?

We assumed 100% of the HCl dissociated!

 $\mathsf{HCI}_{(\mathsf{aq})} \to \mathsf{H^+}_{(\mathsf{aq})} + \, \mathsf{CI^-}_{(\mathsf{aq})}$

That's why 0.1 M HCl gave me 0.1 M $\rm H^{+}$

Suppose only 75% of the HCl dissociated?

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$$\mathsf{HCl}_{(\mathsf{aq})} o \mathsf{H^+}_{(\mathsf{aq})} + \mathsf{Cl^-}_{(\mathsf{aq})}$$

	U.I M	UM	UM
C			
E			

17

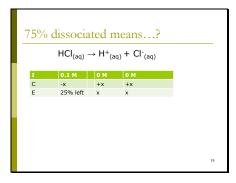
Slide 18

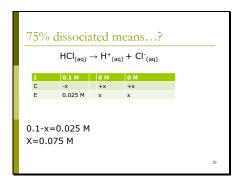
100% dissociated means...?

$$\mathsf{HCI}_{(\mathsf{aq})} o \mathsf{H^+}_{(\mathsf{aq})} + \mathsf{CI^-}_{(\mathsf{aq})}$$

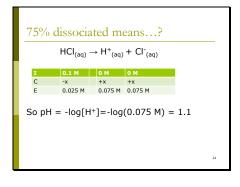
I	0.1 M	0 M	0 M
С	-x	+x	+x
E	0	0.1	0.1

Slide 19





Slide 21



What's my point?

I have several – but one main one:

- 1. pH is NOT NOT NOT the concentration of the acid. It's the concentration of the H+ (or $\rm H_3O^+$ same thing) that fell off the acid.
- 2. To determine the actual pH, I need to know how much acid dissociated.
- 3. ICE charts are good for a lot of different

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Slide 23

So if I'm looking for pH...

...I need to know the H_3O^+ concentration.

The H₃O⁺ concentration WHEN...?

At equilibrium, of course. Before that, the system is n't stable and it is constantly changing.

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Slide 24

Acid Dissociation Reactions

- $\hfill\Box$ This is just a specific type of reaction.
- Referring to Bronsted-Lowry acids: proton donors
- An acid is only an acid when in the presence of a base
- □ Water is the universal base



General Ka Reaction

The general form of this reaction for any generic acid (HA) is:

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Slide 26

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

26

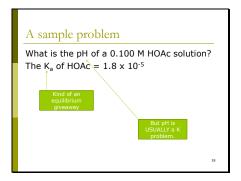
Slide 27

Shorthand Notation

Sometimes the water is left out:

$$\mathsf{HA}_{(\mathsf{aq})} \leftrightarrow \quad \mathsf{A}^{\text{-}}{}_{(\mathsf{aq})} \quad + \quad \mathsf{H}^{\text{+}}{}_{(\mathsf{aq})}$$

This is simpler, but somewhat less precise. It looks like a dissociation reaction, but it doesn't look like an acid/base reaction.



Slide 29

A sample problem

What is the pH of a 0.100 M HOAc solution? The K_a of HOAc = 1.8×10^{-5}

It's just an equilibrium problem. Equilibrium problems have...???

3 FRIGGING PARTS!!!!!!!!

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Old Familiar solution

 $\mathbf{1}^{\text{st}}$ we need a balanced equation:

Slide 31

Old Familiar solution

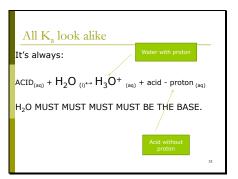
1st we need a balanced equation:

HOAc $_{(aq)}$ + H_2O $_{(I)} \leftrightarrow H_3O^+$ $_{(aq)}$ + $OAc^ _{(aq)}$

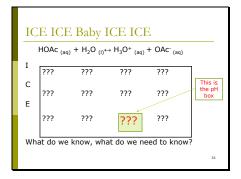
Then we need to construct an ICE chart

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Slide 33







A peek back at the problem.

What is the pH of a 0.100 M HOAc solution? The K_a of HOAc = 1.8 x 10^{-5}

What do we know?

What do we need to know?

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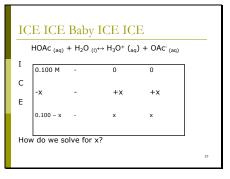
A peek back at the problem.

What is the pH of a 0.100 M HOAc solution? The $\rm K_a$ of HOAc = 1.8 x 10⁻⁵

What do we know? The INITIAL CONCENTRATION of HOAc

What do we need to know? The EQUILIBRIUM CONCENTRATION of ${\rm H_3O^+}$ (Recall, that's what pH is: ${\rm pH} = -\log \ [{\rm H_3O^+}]$





Use the Equilibrium Constant Expression

$$\begin{split} & \text{K}_8 = 1.8 \text{x} 10^{-5} = \underbrace{[\text{H}_3\text{O}^+][\text{A}^-]}_{[\text{HA}]} \\ & 1.8 \text{x} 10^{-5} = \underbrace{[\text{x}][\text{x}]}_{[0.100\text{-x}]} \\ & \text{How do we solve this?} \end{split}$$

Slide 39

2 Possibilities

 $1.8 \times 10^{-5} = \frac{[x][x]}{[0.100-x]}$

- 1. Assume x <<0.100
- 2. Don't assume x << 0.100 and use quadratic formula

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The long way

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1 - x)} = \frac{x^2}{(0.1 - x)}$$

 $x^2 = 1.8 \times 10^{-5} (0.1-x) = 1.8 \times 10^{-6} - 1.8 \times 10^{-5} x$ $x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0$

Recall the quadratic formula: $x = \frac{-b + /- SQRT(b^2-4ac)}{2a}$

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Slide 41

The long way

$$\begin{array}{l} x^2 + 1.8x10^{-5} \, x - 1.8 \, x \, 10^{-6} = 0 \\ x = \frac{-b \, +\!/- \, \text{SQRT} \left(b^2\text{-}4\text{ac}\right)}{2\text{a}} \\ x = \frac{-1.8x10^{-5} \, +\!/- \, \text{SQRT} \left((1.8x10^{-5})^2\text{-}4(1)(-1.8 \, x \, 10^{-6})\right)}{2(1)} \\ x = \left[\frac{-1.8x10^{-5} \, +\!/- \, \text{SQRT} \, \left(7.200x10^{-6}\right)\right]}{2} \\ x = \left[-1.8x10^{-5} \, +\!/- \, 2.68 \, x \, 10^{-3}\right] \end{array}$$

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2 roots - only 1 makes sense

 $x = [-1.8 \times 10^{-5} + /- 2.68 \times 10^{-3}]$

2

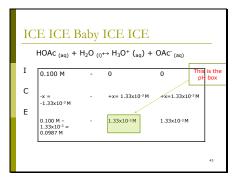
X=1.33x10⁻³ or -1.35x10⁻³

The negative root is clearly non-physical

 $x = 1.33 \times 10^{-3} M$

We can now put this back into the ICE chart

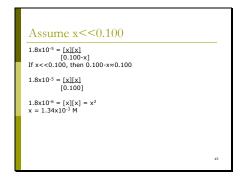
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```
pH = -\log [H_3O^+]
pH = -\log [H_3O^+]
= -\log (1.33x10^{-3})
= 2.88
Was all of that work necessary?
Let's look at making the assumption!
```

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Was the assumption good?

We assumed that x<<0.100, is 1.34x10⁻³ M << 0.100?

 $\frac{0.100}{20} = 0.005$

1.34×10⁻³<0.005
It passes the 5% rule. Notice how little difference it makes in the final answer.

And if I calculate the pH = - log (1.34x10⁻³) pH = 2.87

This compares well with pH = 2.88 calculated the long way. Look at all the work we saved!

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ALL acid dissociation reactions are the same!

Acid + $H_2O \leftrightarrow H_3O^+$ + protonless acid

The ONLY thing that happens in an acid dissociation reaction is that the acid donates its proton to water to make $\rm H_3O^+$.

A single proton hops from the acid to the water.

That's it. ALWAYS.

Anything else, even if there's an acid, is not a K_{a} reaction.

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Base Dissociation Reactions

- □ Acids and bases are matched sets.
- $\hfill \square$ If there is a $K_{a\prime}$ then it only makes sense that there is a K_b
- $\hfill\Box$ The base dissociation reaction is also within the Bronsted-Lowry definition
- □ Water now serves as the acid rather than the base.

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General K_b Reaction

The general form of this reaction for any generic base (B) is:

Looks just like the $\rm K_a$ only the $\rm H^+$ goes the opposite direction (from the water rather than to the water).

Slide 50

K.

It is, after all, just another "K"

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

And this gets used just like any other equilibrium constant expression.

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Slide 51

Question

What is the pH of 0.250 M $\mathrm{NH_{3}}$?

 $K_b (NH_3) = 1.79x10^{-5} at 298 K$

Slide 52	It's an equilibrium questionit's got THREE PARTS!	
Slide 53		
Silue 33	$\begin{tabular}{c} \hline Question \\ \hline What is the pH of 0.250 M NH_3? \\ K_b (NH_3) = 1.79 x 10^{-5} at 298 K \\ NH_{3 (aq)} + H_2O_{(I)} \leftrightarrow NH_4^+_{(aq)} + OH^{(aq)} \\ K_b = \hline{[OH-][NH_4+]}_{[NH_3]} \\ \hline \end{tabular}$	
Slide 54	$\begin{array}{c ccccc} \underline{Question} & & & \\ \hline NH_{3(aq)} + H_{2}O_{(l)} \leftrightarrow NH_{4}{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \\ I \ 0.250 \ M & - & 0 & 0 \\ C - x & - & + x & + x \\ E \ 0.248 & - & x & x \\ \hline K_{b} = \underline{[OH-][NH_{4}{}^{+}]} \\ [NH_{3}] \\ 1.79 \times 10^{-5} = \underline{(x)(x)} \\ & 0.250 - x \\ \hline \end{array}$	

Question

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Question

```
\begin{array}{l} 1.79 \times 10^{-5} = (\textbf{x})(\textbf{x}) \\ 0.250 - \textbf{x} \\ \text{Assume } \textbf{x} < < 0.250 \\ 1.79 \times 10^{-5} = (\textbf{x})(\textbf{x}) \\ 0.250 \\ \textbf{x} = 2.11 \times 10^{-3} = [\text{OH-}] \text{ (good assumption pOH = - log } (2.11 \times 10^{-3}) = 2.67 \\ \text{pOH + pH = 14} \quad (\text{at room temperature}) \\ 14 - \text{pOH = pH} \\ 14 - 2.67 = 11.33 = \text{pH} \end{array}
```

Slide 57

Water, water everywhere

Both K_a and K_b reactions are made possible by the role of water.

Water acts as either an acid or a base. Water is **amphiprotic**.

If water is both an acid and a base, why doesn't it react with itself?

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Water does react with itself

Autoionization of water:

$$H_2O_{(I)}$$
 + $H_2O_{(I)}$ \leftrightarrow $H_3O^+_{(aq)}$ + $OH^-_{(aq)}$

Slide 59

Autoionization of water:

$$\mathrm{H_{2}O}_{\ (I)}\ +\ \mathrm{H_{2}O}_{\ (I)} \leftrightarrow \mathrm{H_{3}O^{+}}_{(aq)}\ +\ \mathrm{OH^{-}}_{(aq)}$$

- $\hfill\Box$ This is, in fact, the central equilibrium in all acid/base dissociations
- \blacksquare This is also the connection between K_{a} and K_{b} reactions.

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The Equilibrium Constant Expression K_w $H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

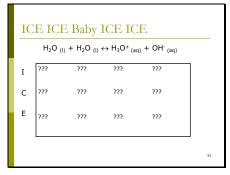
$$H_2O_{(I)} + H_2O_{(I)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

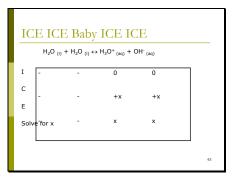
$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

K IS K IS K - this is just another equilibrium constant.

Let's ICE

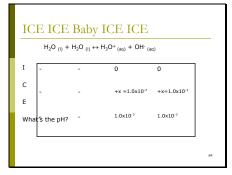
Slide 61





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Evaluating K_w $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ $[x] [x] = 1.0 \times 10^{-14}$ $x^2 = 1.0 \times 10^{-14}$ $x = 1.0x10^{-7}$



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$pH = -\log [H_3O^+]$

 $pH = - log (1.0x10^{-7})$ pH = 7

This is why "7" is considered neutral pH. It is the natural pH of water. Neutral water doesn't have NO acid, it has the EQUILIBRIUM (K_w) amount!!!

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$K_{b}\text{, }K_{a}\text{, and }K_{w}$

It is the Kw of water (1.0×10^{-14}) which is responsible for the observation that: pOH + pH = 14 Since we've already established that pure water has 1×10^{-7} M concentrations of both H+ and OH·

In an aqueous solution, this relationship always holds because K_w must be satisfied even if there are other equilibria that also must be satisfied.

$$\begin{split} &[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \\ &-\text{log}([\text{H}_3\text{O}^+][\text{OH}^-]) = -\text{log}(1.0 \times 10^{-14}) \\ &-\text{log}[\text{H}_3\text{O}^+] + (-\text{log}[\text{OH}^-]) = 14 \\ &\text{pH} + \text{pOH} = 14 \end{split}$$

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K depends on...

...Temperature.

So the "neutral pH" of water is only 7 at STANDARD TEMPERATURE AND PRESSURE!

If the water is at a different temperature, $\rm K_w$ is NOT $\rm 1.0x10^{-14}$

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Slide 69

Backwards and forwards and forwards and back...

The general $K_{\rm a}$ reaction involves donating a proton to water.

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

The acid (HA) is the thing that donates the proton to the base (H_2O).

What if I consider the reverse reaction?

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

What is "A-"?

Yun! It's a base! It got a proton from the H₂O+

•						
	<u> </u>					

Backwards and forwards and forwards and back...

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

What if I consider the reverse reaction?

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

What is "A-"?

Yup! It's a base! It got a proton from the H₃O+ And so, that would make H₃O+...?
Yup! It's an acid! It donated a proton.

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K_b , K_a , and K_w

So, it's really a PAIR of acids and a PAIR of bases!

That means that A- has it's own K_b reaction!

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K_b , K_a , and K_w

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

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

Please note, this general notation can be confusing. I'm referring specifically to the conjugate base of a particular acid. For example: $HOAc\ (aq) + H_2O\ (l) \leftrightarrow OAc^-(aq) + H_3O^+(aq)$

 $OAc^-\left(aq\right) + H_2O\left(l\right) \leftrightarrow HOAc\left(aq\right) + OH^-aq)$

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lid	

Writing the K for both reactions

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

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

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

$$K_b = \frac{[HA][OH-]}{[A-]}$$

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Writing the K for both reactions

If you add these two reactions together

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

$$A^{-} + H_{2}O \leftrightarrow HA + OH^{-}$$

$$HA + A^{-} + H_2O + H_2O \leftrightarrow H_3O^+ + A^{-} + HA^{-} + OH^-$$

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^- OMG! IT'S K_W!!!$$

Slide 75

Add 2 reactions, you multiply the Ks

If you multiply K_a by K_b : $K_a*K_b = \underbrace{[H_2O+][A-]}_{[HA]} \underbrace{[HA][OH-]}_{[A-]}$ $= [H_3O+][OH-]$ $= K_w$

So, if you know $\rm K_b$, you know $\rm K_a$ and vice versa because: $\rm K_a^*K_b\!=\!K_w$

Remember...

 $K_{\rm a}$ and $K_{\rm b}$ refer to specific reactions. I can't just apply them to any old reaction I want.

$$K_w = K_a * K$$

BUT this relationship only holds if the $\rm K_a$ and the $\rm K_b$ are related. It is an acid and its CONJUGATE base (or a base and its CONJUGATE acid).

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 $K_a(HOAc)*K_b(?) = 1x10^{-14}$

It HAS to be the conjugate base.

The conjugate base is ALWAYS just the acid without the $\rm H+$ it donated.

 $HOAc + H_2O \leftrightarrow H_3O^+ + OAc^-$?=OAc^-

Slide 78

 $K_a(?)*K_b(NH_3) = 1x10^{-14}$

It HAS to be the conjugate base.

The conjugate base is ALWAYS just the acid without the H+ it donated. $\label{eq:conjugate} % \begin{subarray}{ll} \end{subarray} % \begin{subar$

 $NH_3 + H_2O \leftrightarrow OH^- + NH_4^+$ $?=NH_4^+$

Remember...

For example, consider the acid dissociation of acetic acid: $HOAc_{(ac)} + H_2O_{(b)} \leftrightarrow H_2O^+_{(ac)} + OAc^-_{(ac)} + OAc^-_{(ac)}$ This reaction has a K_a , it does not have a K_b , BUT, its sister reaction is a base dissociation that has a K_b :

HOAc is an acid OAC- is the CONJUGATE base of HOAc

It is this reaction that you are calculating the K_b for if you use the relationship $K_w = {K_a}^* K_b$