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Chemical Equilibrium
Acids & Bases in Aqueous
Solution

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~~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...

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~~K is K is K is~~
K

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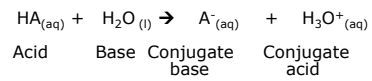
Acid Dissociation Reactions

- 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

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General K_a Reaction

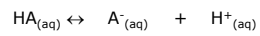
The general form of this reaction for any generic acid (HA) is:



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Shorthand Notation

Sometimes the water is left out:



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

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Familiar Ground

Given this reaction:

$$\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{A}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$$

Can you write the equilibrium constant expression?

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Equilibrium Constant Expression

$$K_a = \frac{[\text{H}_3\text{O}^{+}][\text{A}^{-}]}{[\text{HA}]}$$

NOTE: This is just a K_{eq} , there is nothing new here. It is just a specific type of reaction. So, ICE charts, quadratic formula, etc. all still apply!

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A sample problem

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

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Old Familiar solution

1st we need a balanced equation:

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Old Familiar solution

1st we need a balanced equation:

$$\text{HOAc}_{(aq)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OAc}^-_{(aq)}$$

The we need to construct an ICE chart

$$\text{OAc}^- = \text{C}_2\text{H}_3\text{O}_2^-$$

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ICE ICE Baby ICE ICE

$$\text{HOAc}_{(aq)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OAc}^-_{(aq)}$$

I	???	???	???	???
C	???	???	???	???
E	???	???	???	???

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 K_a of HOAc = 1.8×10^{-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 K_a of HOAc = 1.8×10^{-5}

What do we know? The INITIAL CONCENTRATION of HOAc

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

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ICE ICE Baby ICE ICE

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

I	0.100 M	-	0	0
C	-x	-	+x	+x
E	0.100 - x	-	x	x

How do we solve for x?

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Use the Equilibrium Constant Expression

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.100-x]}$$

How do we solve this?

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2 Possibilities

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

1. Assume $x \ll 0.100$
2. Don't assume $x \ll 0.100$ 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:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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The long way

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

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-6})}}{2(1)}$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{7.200 \times 10^{-6}}}{2}$$

$$x = \frac{-1.8 \times 10^{-5} \pm 2.68 \times 10^{-3}}{2}$$

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2 roots - only 1 makes sense

$$x = \frac{-1.8 \times 10^{-5} \pm 2.68 \times 10^{-3}}{2}$$

The negative root is clearly non-physical

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

We can now put this back into the ICE chart

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ICE ICE Baby ICE ICE

$$\text{HOAc}_{(aq)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OAc}^-_{(aq)}$$

I	0.100 M	-	0	0
C	-x = - 1.33x10 ⁻³ M	-	+x = x = 1.33x10 ⁻³ M	+x = x = 1.33x10 ⁻³ M
E	0.100 M - 1.33x10 ⁻³ = 0.0997 M	-	1.33x10 ⁻³ M	1.33x10 ⁻³ M

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

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (1.33 \times 10^{-3}) \\ &= 2.88\end{aligned}$$

Was all of that work necessary?
Let's look at making the assumption!

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Assume $x \ll 0.100$

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

If $x \ll 0.100$, then $0.100 - x \approx 0.100$

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.100]}$$
$$1.8 \times 10^{-6} = [x][x] = x^2$$
$$x = 1.34 \times 10^{-3} \text{ M}$$

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Was the assumption good?

We assumed that $x \ll 0.100$, is $1.34 \times 10^{-3} \text{ M} \ll 0.100$?
The 1% rule applies and it is very close, but notice how little difference it makes in the final answer?

And if I calculate the $\text{pH} = -\log (1.34 \times 10^{-3})$
 $\text{pH} = 2.87$

This compares well with $\text{pH} = 2.88$ calculated the long way.
Both are $\text{pH} = 2.9$ to 2 sig figs. And look at all the work we saved!

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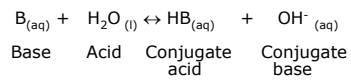
Base Dissociation Reactions

- Acids and bases are matched sets.
- If there is a K_a , then it only makes sense that there is a K_b
- 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:



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K_b

It is, after all, just another "K"

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

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

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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:

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

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Autoionization of water:

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

□ This is, in fact, the central equilibrium in all acid/base dissociations

□ This is also the connection between K_a and K_b reactions.

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The Equilibrium Constant
Expression K_w

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

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

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

Let's ICE

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ICE ICE Baby ICE ICE

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

I	???	???	???	???
C	???	???	???	???
E	???	???	???	???

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ICE ICE Baby ICE ICE

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

I	-	-	0	0
C	-	-	+x	+x
E	-	-	x	x

Solve for x

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Evaluating K_w

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$
$$[x][x] = 1.0 \times 10^{-14}$$
$$x^2 = 1.0 \times 10^{-14}$$
$$x = 1.0 \times 10^{-7}$$

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ICE ICE Baby ICE ICE

$$\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}$$

I	-	-	0	0
C	-	-	+x = 1.0x10 ⁻⁷	+x = 1.0x10 ⁻⁷
E				
What's the pH?	-		1.0x10 ⁻⁷	1.0x10 ⁻⁷

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

$$\text{pH} = -\log (1.0 \times 10^{-7})$$
$$\text{pH} = 7$$

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 , K_a , and K_w

It is the K_w 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.

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$[OH^-][H_3O^+] = 1 \times 10^{-14}$

$-\log([OH^-][H_3O^+]) = -\log 1 \times 10^{-14}$

$-\log[OH^-] + (-\log[H_3O^+]) = 14$

$pOH + pH = 14$

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What is the pH of a 0.050 M solution of formic acid ($HCHO_2$)?

$[K_a = 1.8 \times 10^{-4}]$

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What is the pH of a 0.100 M solution of NH_3 ?
[$K_b = 1.8 \times 10^{-5}$]

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K_b , K_a , and K_w

The general K_a reaction involves donating a proton to water.
 $\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-$
where A^- is the "conjugate base" to HA , and H_3O^+ is the conjugate acid to H_2O .

The general K_b reaction involves accepting a proton from water.
 $\text{A}^- + \text{H}_2\text{O} \leftrightarrow \text{HA} + \text{OH}^-$

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Writing the K for both reactions

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

If you multiply K_a by K_b :

$$K_a \cdot K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$
$$= \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{1}$$
$$= K_w$$

So, if you know K_b , you know K_a and vice versa because:
 $K_a \cdot K_b = K_w$

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Remember...

K_a and K_b refer to specific reactions.

For example, consider the acid dissociation of acetic acid:
 $\text{HOAC}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{OAC}^-_{(aq)}$

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 :

$$\text{OAC}^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{OH}^-_{(aq)} + \text{HOAC}_{(aq)}$$

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

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What is the pH of 0.100 M HCl?

HCl is a strong acid!

What does that mean?

It means it almost completely dissociates.

$$K_a \approx \infty$$
$$[\text{H}_3\text{O}^+] = [\text{HCl}]$$
$$\text{pH} = -\log [0.100 \text{ M}]$$
$$\text{pH} = 1$$

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If you can't find K_a ...

...maybe it's a strong acid.
Or if you do find it, it is HUGE!

Strong acids:

- HCl $K_a \sim 10^6$
- HBr
- HI
- HNO_3
- HClO_4
- H_2SO_4 (diprotic - more on this next week)

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If you can't find a K_b ...
 ...maybe it's a strong base. (Or K_b is huge.)

List of strong bases:
 LiOH
 NaOH $K_b \sim 10^8$
 KOH
 Sr(OH)₂
 Ca(OH)₂
 Ba(OH)₂

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So for a strong acid (or base)

$\text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$
 This reaction has a K_a that is huge (approximately 10^6).
 Its sister reaction (reverse) is a base dissociation that has a K_b :
 $\text{Cl}^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{OH}^-_{(aq)} + \text{HCl}_{(aq)}$
 $K_{eq} = K_a \cdot K_b$
 $K_b = K_{eq}/K_a = 1 \times 10^{-14}/10^6 = 1 \times 10^{-20}$
 It doesn't happen!!!

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So for a strong acid (or base)

IT AIN'T AN EQUILIBRIUM!

$\text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$

I	0.100 M	-	0	0
C	-x	-	+x	+x
E	0	-	0.100 M	0.100 M
