Slide 1

Chemical Equilibrium
Acids & Bases in Aqueous Solution

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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…

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Slide 3

K is K is K is K

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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.

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Slide 5

They go together…like 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.

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Slide 6

What's the most common acid?

Water!!

H-OH, it has a proton it can donate.

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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.

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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.

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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.

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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?

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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

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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 $H^{+\cdot}$

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Slide 13

Example

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

Or, $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

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Slide 14

What is pH?

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

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

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:
       $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Or, $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

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

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Slide 16

We made an assumption?

We assumed 100% of the HCl dissociated!

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

That's why 0.1 M HCl gave me 0.1 M H$^+$

Suppose only 75% of the HCl dissociated?

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Slide 17

75% dissociated means…?

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

I	0.1 M	0 M	0 M
C			
E			

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Slide 18

75% dissociated means…?

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	75% left	x	x

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Slide 19

75% dissociated means…?

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	0.025 M	x	x

0.1-x=0.025 M
X=0.075 M

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Slide 20

75% dissociated means…?

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	0.025 M	0.075 M	0.075 M

So pH = -log[H⁺]=-log(0.075 M) = 1.1

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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 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 things!

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Slide 22

Why would the acid not 100% dissociate?

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Slide 23

So if I'm looking for pH…

…I need to know the H_3O^+ concentration.

The H_3O^+ concentration WHEN…?

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

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Slide 24

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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Slide 25

General K_a Reaction

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

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

Acid   Base   Conjugate   Conjugate
                    base   acid

_____

_____

_____

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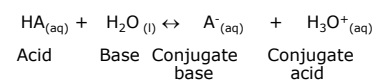
Slide 26

Shorthand Notation

Sometimes the water is left out:

$$HA_{(aq)} \leftrightarrow A^-_{(aq)} + H^+_{(aq)}$$
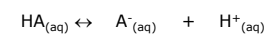
This is simpler, but somewhat less precise. It looks like a dissociation reaction, but it doesn't look like an acid/base reaction.

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Slide 27

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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Slide 28

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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Slide 29

Old Familiar solution

1st we need a balanced equation:

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Slide 30

Old Familiar solution

1st we need a balanced equation:

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

Then we need to construct an ICE chart

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Slide 31

ICE ICE Baby ICE ICE

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

I

???	???	???	???

C

???	???	???	???

E

???	???	???	???

What do we know, what do we need to know?

Slide 32

ICE ICE Baby ICE ICE

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

I

???	???	???	???

C

-x	-x	+x	+x

E

???	???	???	???

What do we know, what do we need to know?

Slide 33

A peek back at the problem.

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

What do we know?

What do we need to know?

Slide 34

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:

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

Slide 35

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?

Slide 36

Use the Equilibrium Constant Expression

$K_a = 1.8 \times 10^{-5} = \dfrac{[H_3O^+][A^-]}{[HA]}$

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

How do we solve this?

Slide 37

2 Possibilities

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

1. Assume $x \ll 0.100$
2. Don't assume $x \ll 0.100$ and use quadratic formula

Slide 38

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:

$$x = \frac{-b +/- \text{SQRT}(b^2 - 4ac)}{2a}$$

Slide 39

The long way

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

$x = \dfrac{-b +/- \text{SQRT}(b^2 - 4ac)}{2a}$

$x = \dfrac{-1.8 \times 10^{-5} +/- \text{SQRT}((1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-6}))}{2(1)}$

$x = \dfrac{[-1.8 \times 10^{-5} +/- \text{SQRT}(7.200 \times 10^{-6})]}{2}$

$x = \dfrac{[-1.8 \times 10^{-5} +/- 2.68 \times 10^{-3}]}{2}$

Slide 40

2 roots - only 1 makes sense

$$x = \frac{[-1.8 \times 10^{-5} +/- 2.68 \times 10^{-3}]}{2}$$

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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Slide 41

ICE ICE Baby ICE ICE

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

I	0.100 M	-	0	0
C	-x = -1.33×10⁻³ M	-	+x=x = 1.33×10⁻³ M	+x=x = 1.33×10⁻³ M
E	0.100 M – 1.33×10⁻³ = 0.0987 M	-	1.33×10⁻³ M	1.33×10⁻³ M

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Slide 42

pH = - log [H₃O⁺]

pH = - log [H_3O^+]
    = - log (1.33×10^{-3})
    = 2.88

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

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Slide 43

Assume x<<0.100

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

If x<<0.100, then 0.100-x≈0.100

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

$1.8 \times 10^{-6} = [x][x] = x^2$

x = 1.34×10^{-3} M

Slide 44

Was the assumption good?

We assumed that x<<0.100, is 1.34×10^{-3} M << 0.100?
The 5% rule applies and it is very close, but notice how little difference it makes in the final answer?

And if I calculate the pH = - log (1.34×10^{-3})
pH = 2.87

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

Slide 45

ALL acid dissociation reactions are the same!

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

The ONLY thing that happens in an acid dissociation reaction is that the acid donates its proton to water to make 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.

Slide 46

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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Slide 47

General K_b Reaction

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

$$B_{(aq)} + H_2O_{(l)} \leftrightarrow HB^+_{(aq)} + OH^-_{(aq)}$$

Base   Acid   Conjugate acid   Conjugate base

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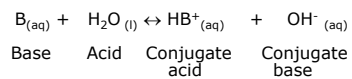
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K_b

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 49

Question

What is the pH of 0.250 M NH_3?

K_b (NH_3) = 1.79×10^{-5} at 298 K

Slide 50

It's an equilibrium question…

…it's got THREE PARTS!

Slide 51

Question

What is the pH of 0.250 M NH_3?
K_b (NH_3) = 1.79×10^{-5} at 298 K

$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$K_b = \dfrac{[OH\text{-}][NH_4^+]}{[NH_3]}$

Slide 52

Question

$$NH_{3\ (aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

I 0.250 M   -   0   0
C −x   -   +x   +x
E 0.250-x   -   x   x

$$K_b = \frac{[OH-][NH_4^+]}{[NH_3]}$$

$$1.79 \times 10^{-5} = \frac{(x)(x)}{0.250-x}$$

Slide 53

Question

$$1.79 \times 10^{-5} = \frac{(x)(x)}{0.250-x}$$

Assume x<<0.250

$$1.79 \times 10^{-5} = \frac{(x)(x)}{0.250} \qquad 4.47 \times 10^{-6} = x^2$$

$x = 2.11 \times 10^{-3} = [OH-]$ (good assumption
$pOH = - \log (2.11 \times 10^{-3}) = 2.67$
$pOH + pH = 14$
$14 - pOH = pH$
$14 - 2.67 = 11.33 = pH$

Slide 54

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?

Slide 55

Water does react with itself

□ Autoionization of water:

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

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Slide 56

Autoionization of water:

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

□ 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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Slide 57

The Equilibrium Constant Expression K_w

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

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

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

Let's ICE

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Slide 58

ICE ICE Baby ICE ICE

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

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

Slide 59

ICE ICE Baby ICE ICE

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

I	-	-	0	0
C				
E	-	-	+x	+x
Solve for x	-		x	x

Slide 60

Evaluating K_w

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

$[x][x] = 1.0 \times 10^{-14}$

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

$x = 1.0 \times 10^{-7}$

Slide 61

ICE ICE Baby ICE ICE

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

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

Slide 62

pH = - log [H$_3$O$^+$]

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!!!

Slide 63

K$_b$, K$_a$, and K$_w$

It is the Kw of water (1.0 x 10^{-14}) which is responsible for the observation that:
pOH + pH = 14
Since we've already established that pure water has 1x10^{-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.

Slide 64

$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$
$-\log([H_3O^+][OH^-]) = -\log(1.0 \times 10^{-14})$
$-\log[H_3O^+] + (-\log[OH-]) = 14$
$pH + pOH = 14$

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Slide 65

Clickers!

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Slide 66

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, K_w
is NOT 1.0×10^{-14}

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Slide 67

K_b, K_a, and K_w

The general K_a reaction involves donating a proton to water.

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

where A- is the "conjugate base" to HA, and H_3O^+ is the conjugate acid to H_2O.

The general Kb reaction involves accepting a proton from water.

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

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Slide 68

Writing the K for both reactions

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

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

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

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

_____

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Slide 69

Writing the K for both reactions

If you add these two reactions together

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

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

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

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

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Slide 70

Add 2 reactions, you multiply the Ks

If you multiply K_a by K_b:

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

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

$$= K_w$$

So, if you know K_b, you know K_a and vice versa because:

$$K_a * K_b = K_w$$

Slide 71

Remember…

K_a and K_b refer to specific reactions. I can't just apply them to any old reaction I want.
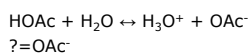
$K_w = K_a * K_b$

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

Slide 72

$K_a(HOAc) * K_b(?) = 1 \times 10^{-14}$

It HAS to be the conjugate base.

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

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

$? = OAc^-$

Slide 73

$K_a(?) * K_b(NH_3) = 1 \times 10^{-14}$

It HAS to be the conjugate base.

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

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

Slide 74

Remember…

For example, consider the acid dissociation of acetic acid:
$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

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:

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

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 $K_w = K_a * K_b$