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MORE ACIDS AND BASES

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Let's try another little problem:

What is the pH of 0.123 M formic acid (HCHO_2)?

$K_a(\text{HCHO}_2) = 1.8 \times 10^{-4}$

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Why don't I write it as CH_2O_2 ?

I could, same molecule, but by writing it HCHO_2 I'm doing two things:

1. I'm emphasizing it's an acid by putting the "H" out front.
2. I'm indicating that only ONE "H" can come off the molecule.

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Not all H's are "acidic"

CH₄ – methane

It's got 4 hydrogens...none of them are considered to be "acidic" because they don't easily come off.

Generally, acids have the "H" bonded to something more electronegative like "O" or a halogen.

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H-O-H (acidic – H bonded to O)
H-Cl (acidic – H bonded to halogen)
H-S-H (acidic – H bonded to S)
H-C... (not acidic – H bonded to C)

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Let's try another little problem:

What is the pH of 0.123 M formic acid (HCHO₂)?

$K_a(\text{HCHO}_2) = 1.8 \times 10^{-4}$

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The 1st thing we need is...

A BALANCED EQUATION!

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HCHO₂

What does the formic acid react with?

H₂O

How do you even know there's water?
It's a solution! (M)

What happens in the reaction?

A proton moves from the acid (HCHO₂) to the base (H₂O):
 $\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

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Once I have a balanced equation:

$\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

2 more parts:

2. K equation
3. Ice chart!

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K equation:

$$\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

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ICE-ICE-BABY-ICE-ICE

$$\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

I					
C					
E					

What do I know?
 "I" of HCHO_2 is 0.123 M
 I always know the "C" line!

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Let's try another little problem:

What is the pH of 0.123 M formic acid (HCHO_2)?

$K_a(\text{HCHO}_2) = 1.8 \times 10^{-4}$

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ICE-ICE-BABY-ICE-ICE

$\text{HCHO}_2 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{CHO}_2^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$

I	0.123 M	-	0	0
C	-x	-x	+x	+x
E	0.123 M	-	x	x

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$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

$$K_a = \frac{[x][x]}{0.123 - x} = 1.8 \times 10^{-4}$$

Always worth trying the assumption
 $x \ll 0.123$

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$$\frac{[x][x]}{0.123 - x} = 1.8 \times 10^{-4}$$

Always worth trying the assumption
 $x \ll 0.123$

$$\frac{[x][x]}{0.123} = 1.8 \times 10^{-4}$$

$$x = \sqrt{0.123 \times 1.8 \times 10^{-4}} = 4.7 \times 10^{-3}$$

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$$x = \sqrt{0.123 \times 1.8 \times 10^{-4}} = 4.7 \times 10^{-3}$$

Good assumption?

$$\frac{0.123}{20} = 6.15 \times 10^{-3}$$

$4.7 \times 10^{-3} < 6.15 \times 10^{-3}$ so it's a good assumption! (although it's close)

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ICE-ICE-BABY-ICE-ICE

$$\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

I	0.123 M	-	0	0
C	-0.0047	-x	+0.0047	+0.0047
E	0.118 M	-	0.0047	0.0047

$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0047 \text{ M}) = 2.33$

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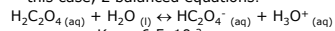
Sample Problem

Calculate the pH of a $1 \times 10^{-3} \text{ M}$ solution of oxalic acid.

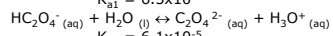
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Solution

As always, we 1st need a balanced equation. Or, in this case, 2 balanced equations!



$$K_{a1} = 6.5 \times 10^{-2}$$

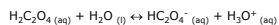


$$K_{a2} = 6.1 \times 10^{-5}$$

2 Equilibria = 2 ICE charts!

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Just take them 1 at a time...



I

C

E

1×10^{-3}	-	0	0
-x	-	+x	+x
1×10^{-3}	-	x	x
-x			

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$$K_{a1} = 6.5 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

$$= \frac{(x)(x)}{1 \times 10^{-3} - x}$$

Try $x \ll 1 \times 10^{-3}$

$$6.5 \times 10^{-2} = \frac{(x)(x)}{1 \times 10^{-3} - x} \approx \frac{x^2}{1 \times 10^{-3}}$$

$$6.5 \times 10^{-5} = x^2$$

$x = 8.06 \times 10^{-3}$ which is NOT much less than 1×10^{-3}

We have to do it the Quadratic Way!

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$$K_{a1} = 6.5 \times 10^{-2} = \frac{(x)(x)}{1 \times 10^{-3} - x}$$

$$6.5 \times 10^{-5} - 6.5 \times 10^{-2} x = x^2$$

$$0 = x^2 + 6.5 \times 10^{-2} x - 6.5 \times 10^{-5}$$

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

$$x = \frac{-6.5 \times 10^{-2} \pm \sqrt{(6.5 \times 10^{-2})^2 - 4(1)(-6.5 \times 10^{-5})}}{2(1)}$$

$$x = \frac{-6.5 \times 10^{-2} \pm \sqrt{4.485 \times 10^{-3}}}{2}$$

$$x = \frac{-6.5 \times 10^{-2} \pm 6.697 \times 10^{-2}}{2}$$

$$x = 9.85 \times 10^{-4} \text{ M}$$

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Finish the first one...

$$\text{H}_2\text{C}_2\text{O}_4 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \leftrightarrow \text{HC}_2\text{O}_4^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$$

	1×10^{-3}	-	0	0
I				
C	-9.85×10^{-4}	-	$+9.85 \times 10^{-4}$	$+9.85 \times 10^{-4}$
E	1.49×10^{-5}	-	9.85×10^{-4}	9.85×10^{-4}

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...and start the second one.

$$\text{HC}_2\text{O}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \leftrightarrow \text{C}_2\text{O}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$$

	9.85×10^{-4}	-	0	9.85×10^{-4}
I				
C	$-x$	-	$+x$	$+x$
E	$9.85 \times 10^{-4} - x$	-	x	$9.85 \times 10^{-4} + x$

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$$K_{a2} = 6.1 \times 10^{-5} = \frac{[H_2O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$= \frac{(x)(9.85 \times 10^{-4} + x)}{9.85 \times 10^{-4} - x}$$

Let's try $x \ll 9.85 \times 10^{-4}$

$$6.1 \times 10^{-5} = \frac{(x)(9.85 \times 10^{-4} + x)}{9.85 \times 10^{-4} - x}$$

$$\approx \frac{x(9.85 \times 10^{-4})}{9.85 \times 10^{-4}}$$

$6.1 \times 10^{-5} = x$
 6.1×10^{-5} is NOT much less than 9.85×10^{-4}

Dang it all!

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$$K_{a2} = 6.1 \times 10^{-5} = \frac{[H_2O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$= \frac{(x)(9.85 \times 10^{-4} + x)}{9.85 \times 10^{-4} - x}$$

$$6.0085 \times 10^{-8} - 6.1 \times 10^{-5} x = 9.85 \times 10^{-4} x + x^2$$

$$0 = x^2 + 1.046 \times 10^{-3} x - 6.0085 \times 10^{-8}$$

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

$$x = \frac{-1.046 \times 10^{-3} \pm \sqrt{(1.046 \times 10^{-3})^2 - 4(1)(-6.0085 \times 10^{-8})}}{2(1)}$$

$$x = \frac{-1.046 \times 10^{-3} \pm \sqrt{1.334 \times 10^{-6}}}{2}$$

$$x = \frac{-1.046 \times 10^{-3} \pm 1.155 \times 10^{-3}}{2}$$

$$x = 5.46 \times 10^{-5} \text{ M}$$

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Finishing up...

$$HC_2O_4^- (aq) + H_2O (l) \leftrightarrow C_2O_4^{2-} (aq) + H_3O^+ (aq)$$

I	9.85×10^{-4}	-	0	9.85×10^{-4}
C	-5.46×10^{-5}	-	$+5.46 \times 10^{-5}$	$+5.46 \times 10^{-5}$
E	9.304×10^{-4}	-	5.46×10^{-5}	1.04×10^{-3}

Clearly, the 2nd equilibrium makes a big difference here.

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Do I need to do this for all acids and bases?

Most, but not all.

There is a distinction between a "strong acid" and a "weak acid". (Or, a "strong base" and a "weak base".

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"strong" isn't STRONG, it's "complete"

Would you rather drink a strong acid or a weak acid?

Depends on the concentration.

"strong" = complete dissociation

"weak" = partial dissociation

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Strong = " \rightarrow "

Weak = " \rightleftharpoons "

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

Complete dissociation means it all reacts so there is ZERO HA left. In other words, K_a is HUGE

Partial dissociation means there is some HA left. In other words, K_a is a number.

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Appendix II (your BEST friend)

If you look at the Table of K_a in Appendix II you'll see numbers from 10^{-1} down to 10^{-13} . All are "weak acids".

If you look on page 665, you'll see a short list of "strong acids". These actually have K_a of 10^6 or higher. They are soooo big, they are usually considered infinite.

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Strong Acids

H_2SO_4
 HNO_3
 HCl
 $HClO_4$
 HBr
 HI

H with a big electronegative group.

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Strong Bases (p. 682)

$LiOH$
 $NaOH$
 KOH
 $Sr(OH)_2$
 $Ca(OH)_2$
 $Ba(OH)_2$

Alkali metals (hey! Where'd the name come from! ☺) with hydroxide ions.

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Question

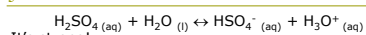
What is the pH of 1×10^{-8} M H_2SO_4 ?

$K_{a1} = \text{infinite}$

$K_{a2} = 1.0 \times 10^{-2}$

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Just take them 1 at a time...

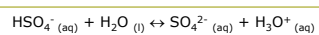


It's strong!

I	1×10^{-8}	-	0	0
C	-x	-	+x	+x
E	0	-	1×10^{-8}	1×10^{-8}

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2nd one starts where 1st one ends!



I	1×10^{-8}	-	0	1×10^{-8}
C	-x	-	+x	+x
E	$1 \times 10^{-8} - x$	-	x	$1 \times 10^{-8} + x$

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$$K_{a2} = 1.0 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

$$1.0 \times 10^{-2} = \frac{(1 \times 10^{-8} + x)(x)}{(1 \times 10^{-8} - x)}$$

Can we assume $x \ll 0.100$?
Never hurts to try.

$$1.0 \times 10^{-2} = \frac{(1 \times 10^{-8})(x)}{(1 \times 10^{-8})}$$

$x = 1.0 \times 10^{-2}$ which is NOT much less than 1×10^{-8}

We have to do it the Quadratic Way!

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$$K_{a2} = 1.0 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

$$1.0 \times 10^{-2} = \frac{(1 \times 10^{-8} + x)(x)}{(1 \times 10^{-8} - x)}$$

$$1.0 \times 10^{-10} - 1.0 \times 10^{-2} x = 1.0 \times 10^{-8} x + x^2$$

$$0 = x^2 + 1.000001 \times 10^{-2} x - 1.0 \times 10^{-10}$$

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

$$x = \frac{-1.000001 \times 10^{-2} \pm \sqrt{(1.000001 \times 10^{-2})^2 - 4(1)(-1.0 \times 10^{-10})}}{2(1)}$$

$$x = \frac{-1.000001 \times 10^{-2} \pm \sqrt{1.000006 \times 10^{-4}}}{2}$$

$$x = \frac{-1.000001 \times 10^{-2} \pm 1.000003 \times 10^{-2}}{2}$$

$$x = \frac{1.999996 \times 10^{-8}}{2}$$

$$X = 9.99998 \times 10^{-9} = 1 \times 10^{-8}$$

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Finish off the 2nd one!

$$\text{HSO}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \leftrightarrow \text{SO}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$$

I	1×10^{-8}	-	0	1×10^{-8}
C				
E	-1×10^{-8}	-	$+1 \times 10^{-8}$	$+1 \times 10^{-8}$
	$1 \times 10^{-8} - x$	-	1×10^{-8}	2×10^{-8}

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AND START THE
3RD ONE!!!!!!

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VERY dilute acid – can't ignore K_w

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

I

C

E

-	-	0	2×10^{-8}
-	-	$+x$	$+x$
-	-	x	$2 \times 10^{-8} + x$

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$$K_w = 1.0 \times 10^{-14} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{(2.0 \times 10^{-8} + x)(x)}$$

$$1.0 \times 10^{-14} = 2.0 \times 10^{-8} x + x^2$$

$$0 = x^2 + 2.0 \times 10^{-8} x - 1.0 \times 10^{-14}$$

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

$$x = \frac{-2.0 \times 10^{-8} \pm \sqrt{(2.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = \frac{-2.0 \times 10^{-8} \pm \sqrt{4.04 \times 10^{-14}}}{2}$$

$$x = \frac{-2.0 \times 10^{-8} \pm 2.00998 \times 10^{-7}}{2}$$

$$x = 1.809975 \times 10^{-7}$$

$$x = 9.04988 \times 10^{-8} = 9.05 \times 10^{-8}$$

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Finish off K_w

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

I	-	-	0	2×10^{-8}
C	-	-	$+9.05 \times 10^{-8}$	$+9.05 \times 10^{-8}$
E	-	-	9.05×10^{-8}	1.105×10^{-7}

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

$$\text{pH} = -\log(1.105 \times 10^{-7})$$

$$\text{pH} = 6.96$$

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Suppose you have a really, really dilute acid...say 1×10^{-7} M HCl, what's the pH?

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What do we know about HCl?

It's a really strong acid!

Suppose I had 0.100 M HCl, what's the pH?

- A. pH = 0.1
- B. pH = 1.0
- C. pH = -1.0
- D. pH = 2.3
- E. I'm still thinking about the test...

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Strong acids, completely dissociate

$\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$			
I	Y	-	0
C	-x	-	+x
E	0	Y	Y

So 0.100 M HCl yields 0.100 M H_3O^+ .
 $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.100) = 1.0$

(I don't even need the ICE chart ☺)

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What is the pH of 1×10^{-7} M HCl?

HCl is still a strong acid, so it completely dissociates.

1×10^{-7} M HCl gives you 1×10^{-7} M H_3O^+
 $\text{pH} = -\log(1 \times 10^{-7}) = 7$

Is that it, are we done? A really dilute acid is neutral. Seems reasonable.

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There is another equilibrium!

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

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

And H_3O^+ is part of it!

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

I	-	-	1×10^{-7}	0
C	-X	-X	+X	+X
E	-	-	$1.0 \times 10^{-7} + x$	x

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

$$1.0 \times 10^{-14} = (1.0 \times 10^{-7} + x)(x)$$

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

I	-	-	1×10^{-7}	0
C	-X	-X	$+6.18 \times 10^{-8}$	$+6.18 \times 10^{-8}$
E	-	-	1.62×10^{-7}	$+6.18 \times 10^{-8}$

$\text{pH} = -\log(1.62 \times 10^{-7})$
 $\text{pH} = 6.8$

Compared to 1×10^{-7} and $\text{pH} = 7$ for the HCl alone

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When do I need to consider K_w ?

1. The acid is very dilute
2. The acid is very weak (K_a less than 10^{-12})
3. Both 1 and 2

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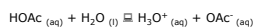
A very weak acid problem

What is the pH of a 1×10^{-7} M solution of HOAc?

$$K_{a,\text{HOAc}} = 1.8 \times 10^{-5}$$

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ICE ICE Baby ICE ICE



I	1×10^{-7}	-	0	0
C	-x	-	+x	+x
E	$1 \times 10^{-7} - x$	-	x	x

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K_a

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{OAc}^-][\text{H}_3\text{O}^+]}{[\text{HOAc}]}$$

$$= \frac{(x)(x)}{(1 \times 10^{-7} - x)}$$

$$= \frac{x^2}{(1 \times 10^{-7} - x)}$$

I will not assume x is small since 1×10^{-7} is pretty small itself

$$1.8 \times 10^{-12} - 1.8 \times 10^{-5} x = x^2$$

$$0 = x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-12}$$

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Solving for x

$$0 = x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-12}$$

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

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-12})}}{2(1)}$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} + 7.2 \times 10^{-12}}}{2}$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{3.312 \times 10^{-10}}}{2}$$

$$x = \frac{-1.8 \times 10^{-5} \pm 1.8199 \times 10^{-5}}{2}$$

$$x = 9.95 \times 10^{-6} \text{ M}$$

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Suppose I already have $1 \times 10^{-7} \text{ M } [\text{H}_3\text{O}^+]$ from the K_w ?

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

I	1×10^{-7}	-	1×10^{-7}	0
C	-x	-	+x	+x
E	$1 \times 10^{-7} - x$	-	$1 \times 10^{-7} + x$	x

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K_a

$$K_a = 1.8 \times 10^{-5} = \frac{[OAc^-][H_3O^+]}{[HOAc]}$$

$$K_a = 1.8 \times 10^{-5} = \frac{[x][1 \times 10^{-7} + x]}{[1 \times 10^{-7} - x]}$$

$$1.8 \times 10^{-12} - 1.8 \times 10^{-5} x = x^2 + 1 \times 10^{-7} x$$

$$0 = x^2 + 1.81 \times 10^{-5} x - 1.8 \times 10^{-12}$$

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Solving for x

$$0 = x^2 + 1.81 \times 10^{-5} x - 1.8 \times 10^{-12}$$

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

$$x = \frac{-1.81 \times 10^{-5} \pm \sqrt{(1.81 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-12})}}{2(1)}$$

$$x = \frac{-1.81 \times 10^{-5} \pm \sqrt{3.276 \times 10^{-10} + 7.2 \times 10^{-12}}}{2}$$

$$x = \frac{-1.81 \times 10^{-5} \pm \sqrt{3.348 \times 10^{-10}}}{2}$$

$$x = \frac{-1.81 \times 10^{-5} \pm 1.8298 \times 10^{-5}}{2}$$

$$x = 9.88 \times 10^{-6} \text{ M}$$

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But I already have $1 \times 10^{-7} \text{ M } [H_3O^+]$ from the K_w before I even add the HOAc

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

I	$1 \times 10^{-7} \text{ M}$	-	$1 \times 10^{-7} \text{ M}$	0
C	$-9.88 \times 10^{-6} \text{ M}$	-	$+9.88 \times 10^{-6} \text{ M}$	$+9.88 \times 10^{-6} \text{ M}$
E		-	$1.98 \times 10^{-6} \text{ M}$	$9.88 \times 10^{-6} \text{ M}$

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Comparing the 2 numbers

- Without considering K_w , I calculate from K_a :

$$[\text{H}_3\text{O}^+] = 9.95 \times 10^{-8} \text{ M}$$

- Considering K_w and K_a , I calculate:

$$[\text{H}_3\text{O}^+] = 1.988 \times 10^{-7} \text{ M}$$

A significant difference!!
