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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 ($HCHO_2$)?

$K_a(HCHO_2) = 1.8x10^{-4}$

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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"

CH_4 – methane

It has 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 ($HCHO_2$)?
$K_a(HCHO_2) = 1.8\times10^{-4}$

A. 2.03
B. 3.74
C. -1.41
D. 2.33
E. I have no clue

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The 1st thing we need is…

A BALANCED EQUATION!

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HCHO$_2$

What does the formic acid react with?

H_2O

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

What happens in the reaction?

A proton moves from the acid ($HCHO_2$) to the base (H_2O):
$HCHO_2$ (aq) + H_2O (l) ↔ CHO_2^- (aq) + H_3O^+(aq)

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Once I have a balanced equation:

$HCHO_2$ (aq) + H_2O (l) ↔ CHO_2^- (aq) + H_3O^+(aq)

2 more parts:
2. K equation
3. Ice chart!

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K equation:

$HCHO_2$ (aq) + H_2O (l) ↔ CHO_2^- (aq) + H_3O^+(aq)

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]}$$

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ICE-ICE-BABY-ICE-ICE

$HCHO_2$ (aq) + H_2O (l) ↔ CHO_2^- (aq) + H_3O^+(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 ($HCHO_2$)?

$K_a(HCHO_2)$ = 1.8×10^{-4}

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ICE-ICE-BABY-ICE-ICE

$HCHO_2\ (aq) + H_2O\ (l) \leftrightarrow CHO_2^-\ (aq) + H_3O^+(aq)$

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

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$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]}$$
$$K_a = \frac{[x][x]}{0.123 - x} = 1.8 \times 10^{-4}$$

Always worth trying the assumption
X<<0.123

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

Always worth trying the assumption
X<<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?

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

$4.7\times10^{-3} < 6.15\times10^{-3}$ so it's a good assumption! (although it's close)

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ICE-ICE-BABY-ICE-ICE

$HCHO_2$ (aq) + H_2O (l) ↔ CHO_2^- (aq) + H_3O^+(aq)

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

pH=-log[H_3O^+]=-log(0.0047 M) = 2.33

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Sample Problem

Calculate the pH of a 1×10^{-3} 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!

$H_2C_2O_4\,_{(aq)} + H_2O\,_{(l)} \leftrightarrow HC_2O_4^-\,_{(aq)} + H_3O^+\,_{(aq)}$

$K_{a1} = 6.5\times10^{-2}$

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

$K_{a2} = 6.1\times10^{-5}$

2 Equilbria = 2 ICE charts!

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Polyprotic Acids (or bases)

- Some acids are capable of donating more than one proton
- Some bases are capable of accepting more than one proton

When this occurs, you will have more than one equilibrium to consider

[YAY! We love equilibrium!]

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How would you know it's a polyprotic acid?

2 ways:

1. Chemical formula
2. K_a (or K_b for bases):

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Some Polyprotic Acids

- H_2SO_4 – sulfuric acid
- H_2SO_3 – sulfurous acid
- H_3PO_4 – phosphoric acid
- $H_2C_2O_4$ – oxalic acid
- H_2S – hydrosulfuric acid
- H_2CO_3 – carbonic acid

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K_a

If you look up the acid on the table of K_a values, it will have more than one K_a!

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Sample Problem

Calculate the pH of a $1x10^{-3}$ 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!

$H_2C_2O_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrow HC_2O_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

$K_{a1} = 6.5x10^{-2}$

$HC_2O_4^-{}_{(aq)} + H_2O_{\,(l)} \leftrightarrow C_2O_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

$K_{a2} = 6.1x10^{-5}$

2 Equilibria = 2 ICE charts!

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Just take them 1 at a time…

$H_2C_2O_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrow HC_2O_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

I	$1x10^{-3}$	-	0	0
C	-x	-	+x	+x
E	$1x10^{-3}$ -x	-	x	x

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$K_{a1} = 6.5x10^{-2} = \frac{[H_3O+][HC_2O_4^-]}{[H_2C_2O_4]}$

$= \frac{(x)(x)}{1\times10^{-3}-x}$

Try $x<<1x10^{-3}$

$$6.5x10-2 = \frac{(x)(x)}{1\times10^{-3}-x} \approx \frac{x^2}{1\times10^{-3}}$$

$6.5x10^{-5} = x^2$

$x= 8.06x10^{-3}$ which is NOT much less than $1x10^{-3}$

We have to do it the Quadratic Way!

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

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

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

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

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

$$x = \frac{-6.5 \times 10^{-2} \pm \sqrt{4.485 \times 10^{-3}}}{2} = \frac{-6.5 \times 10^{-2} \pm 6.697 \times 10^{-2}}{2}$$

$$x = 9.85 \times 10^{-4}\ OR\ -0.066$$

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Finish the first one…

$H_2C_2O_{4\,(aq)} + H_2O_{(l)} \leftrightarrow HC_2O_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

I	$1x10^{-3}$	-	0	0
C	$- 9.85x10^{-4}$	-	$+9.85x10^{-4}$	$+9.85x10^{-4}$
E	$1.49x10^{-5}$	-	$9.85x10^{-4}$	$9.85x10^{-4}$

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…and start the second one.

$HC_2O_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow C_2O_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

I	$9.85x10^{-4}$	-	0	$9.85x10^{-4}$
C	-x	-	+x	+x
E	$9.85x10^{-4}$ - x	-	x	$9.85x10^{-4}$ + x

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$$K_{a2} = 6.1x10-5 = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$= \frac{(x)(9.85\times10^{-4}+x)}{9.85\times10^{-4}-x}$$

Let's try x<< $9.85x10^{-4}$

$$6.1x10-5 = \frac{(x)(9.85\times10^{-4}+x)}{9.85\times10^{-4}-x}$$

$$\approx \frac{x(9.85\times10^{-4})}{9.85\times10^{-4}}$$

$6.1x10^{-5}$ = x

$6.1x10^{-5}$ is NOT much less than $9.85x10^{-4}$

Dang it all!

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$$K_{a2} = 6.1\times10^{-5} = \frac{[H_3O+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$6.1x10^{-5} = \frac{(x)(9.85x10-4+x)}{9.85x10-4-x}$$

$6.0085x10^{-8}$ – $6.1x10^{-5}$ x = $9.85x10^{-4}$ x + x^2

0 = x^2 + $1.046x10^{-3}$ x – $6.0085x10^{-8}$

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

$$x = \frac{-1.046\times10^{-3} \pm \sqrt{(1.046\times10^{-3})^2-4(1)(-6.0085\times10^{-8})}}{2(1)}$$

$$x = \frac{-1.046\times10^{-3} \pm 1.155\times10^{-3}}{2}$$

$$x = 5.46\times10^{-5}\ OR\ -1.1\times10^{-3}$$

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Finishing up…

$HC_2O_4^-{}_{(aq)}$ + $H_2O_{(l)}$ ↔ $C_2O_4^{2-}{}_{(aq)}$ + $H_3O^+{}_{(aq)}$

I	$9.85x10^{-4}$	-	0	$9.85x10^{-4}$
C	- $5.46x10^{-5}$	-	+$5.46x10^{-5}$	+$5.46x10^{-5}$
E	$9.304x10^{-4}$	-	$5.46x10^{-5}$	$1.04x10^{-3}$

Clearly, the 2nd equilibrium makes a big difference here.
pH=-log($1.04x10^{-3}$) = 2.983

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

A. Strong
B. Weak
C. Neither
D. It's a flawed question.

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$HA + H_2O = A^- + H_3O^+$

Strong = "→" Weak = "↔"

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

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

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Just take them 1 at a time…

$H_2SO_{4\,(aq)} + H_2O_{(l)} \leftrightarrow HSO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

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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2^{nd} one starts where 1^{st} one ends!

$HSO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow SO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

	HSO_4^-	H_2O	SO_4^{2-}	H_3O^+
I	$1x10^{-8}$	-	0	$1x10^{-8}$
C	-x	-	+x	+x
E	$1x10^{-8}$ - x	-	x	$1x10^{-8}$ +x

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$K_{a2} = 1.0x10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$

$1.0x10^{-2} = \frac{(1x10^{-8}+x)(x)}{(1x10^{-8}-x)}$

Can we assume $x<<1x10^{-8}$??
Never hurts to try.

$1.0x10^{-2} = \frac{(1x10^{-8})(x)}{(1x10^{-8})}$

$x=1.0x10^{-2}$ which is NOT much less than $1x10^{-8}$

We have to do it the Quadratic Way!

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$K_{a2} = 1.0x10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$

$1.0x10^{-2} = \frac{(1x10^{-8}+x)(x)}{(1x10^{-8}-x)}$

$1.0x10^{-10} – 1.0x10^{-2} x = 1.0x10^{-8} x + x2$

$0 = x^2 + 1.000001x10^{-2} x – 1.0x10^{-10}$

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

$x = \frac{- 1.000001x10^{-2} +/- SQRT((1.000001x10^{-2})^2-4(1)(– 1.0x10^{-10}))}{2(1)}$

$x = \frac{- 1.000001x10^{-2} +/- SQRT(1.000006x10^{-4})}{2}$

$x = \frac{- 1.000001x10^{-2} +/- 1.000003x10^{-2}}{2}$

$x = \frac{1.999996x10^{-8}}{2}$

$X=9.99998x10^{-9} = 1x10^{-8}$

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Finish off the 2nd one!

$HSO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow SO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

I	$1x10^{-8}$	-	0	$1x10^{-8}$
C	$-1x10^{-8}$	-	$+1x10^{-8}$	$+1x10^{-8}$
E	$1x10^{-8}$ - x	-	$1x10^{-8}$	$2x10^{-8}$

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pH=-log($2x10^{-8}$)
pH=7.699

- How do you feel about that?
- A. Happy
- B. Sad
- C. Confused
- D. Mad
- E. what the hell kind of question is that?

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

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VERY dilute acid – can't ignore K_w

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

I	-	-	0	$2x10^{-8}$
C	-	-	+x	+x
E	-	-	x	$2x10^{-8}$+x

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$K_w = 1.0x10^{-14} = [H_3O^+][OH^-] = (2.0x10^{-8} + x)(x)$

$1.0x10^{-14} = 2.0x10^{-8}\ x + x^2$

$0 = x^2 + 2.0x10^{-8}\ x - 1.0x10^{-14}$

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

$x = \frac{-2.0x10^{-8} +/- SQRT((2.0x10^{-8})^2-4(1)(-1.0x10^{-14}))}{2(1)}$

$x = \frac{-2.0x10^{-8} +/- SQRT(4.04x10^{-14})}{2}$

$x = \frac{-2.0x10^{-8} +/- 2.00998x10^{-7}}{2}$

$x = \frac{1.809975x10^{-7}}{2}$

$X = 9.04988x10^{-8} = 9.05x10^{-8}$

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Finish off K_w

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

I	-	-	0	$2x10^{-8}$
C	-	-	$+9.05x10^{-8}$	$+9.05x10^{-8}$
E	-	-	$9.05x10^{-8}$	$1.105x10^{-7}$

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`

$pH = - \log[H_3O^+]$
$pH = - \log (1.105x10^{-7})$
$pH = 6.96$

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Suppose you have a really, really dilute acid…say $1x10^{-7}$ MHCl, 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?

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Strong acids, completely dissociate

	HCl	+ H_2O ↔	H_3O^+	+ Cl^-
I	Y	-	0	0
C	-x	-	+x	+x
E	0		Y	Y

So 0.100 M HCl yields 0.100 M H_3O^+.
pH = $-\log[H_3O^+]$ = - 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^+
pH = - log (1×10^{-7}) = 7

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

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There is another equilibrium!

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$
$K_w = 1.0 \times 10^{-14}$

And H_3O^+ is part of it!

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

I	-	-		$1X10^{-7}$	0
C	-X	-X		+X	+X
E	-	-		$1.0x10^{-7}$ +x	x

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

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

I	-	-		$1X10^{-7}$	0
C	-X	-X		$+6.18x10^{-8}$	$+6.18x10^{-8}$
E	-	-		$1.62x10^{-7}$	$+6.18x10^{-8}$

pH = - log ($1.62x10^{-7}$)
pH = 6.8

Compared to $1x10^{-7}$ and 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?

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

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ICE ICE Baby ICE ICE

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

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

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K_a

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

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

I will not assume x is small since 1×10^{-7} is pretty small itself (you could try it)

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

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

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Solving for x

$0 = x^2 + 1.8\times10^{-5}\,x - 1.8\times10^{-12}$

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

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2-4(1)(-1.8\times10^{-12})}}{2(1)}$$

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{3.24\times10^{-10}+7.2\times10^{-12}}}{2}$$

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{3.312\times10^{-10}}}{2}$$

$$x = \frac{-1.8\times10^{-5} \pm 1.8199\times10^{-5}}{2}$$

$x = 9.95\times10^{-8}$ M

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Suppose I already have 1×10^{-7} M $[H_3O^+]$ from the K_w?

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

	HOAc	H_2O	H_3O^+	OAc^-
I	1×10^{-7}	-	1×10^{-7}	0
C	-x	-	+x	+x
E	1×10^{-7} -x	-	1×10^{-7} + x	x

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K_a

$$K_a = 1.8\times10^{-5} = \frac{[OAc^-][H_3O^+]}{[HOAc]}$$

$$K_a = 1.8\times10^{-5} = \frac{[x][1\times10^{-7}+x]}{[1\times10^{-7}-x]}$$

$1.8\times10^{-12} - 1.8\times10^{-5}\,x = x^2 + 1\times10^{-7}\,x$

$0 = x^2 + 1.81\times10^{-5}\,x - 1.8\times10^{-12}$

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Solving for x

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

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

$x = \dfrac{-\,1.81\text{x}10^{-5} +/- \text{SQRT}((1.81\text{x}10^{-5})^2 - 4(1)(-\,1.8\text{x}10^{-12}))}{2(1)}$

$x = \dfrac{-\,1.81\text{x}10^{-5} +/- \text{SQRT}(3.276\text{x}10^{-10} + 7.2\text{x}10^{-12})}{2}$

$x = \dfrac{-\,1.81\text{x}10^{-5} +/- \text{SQRT}(3.348\text{x}10^{-10})}{2}$

$x = \dfrac{-\,1.81\text{x}10^{-5} +/- 1.8298\text{x}10^{-5}}{2}$

$x = 9.88\ \text{x}10^{-8}$ M

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But I already have $1\text{x}10^{-7}$ 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	$1\text{x}10^{-7}$ M	-	$1\text{x}10^{-7}$ M	0
C	$-\ 9.88\ \text{x}10^{-5}$M	-	$+9.88\ \text{x}10^{-8}$M	$+9.88\ \text{x}10^{-8}$ M
E		-	$1.98\text{x}10^{-8}$ M	$9.88\ \text{x}10^{-8}$ M

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Comparing the 2 numbers

- Without considering K_w, I calculate from K_a:

  $[H_3O^+] = 9.95\ \text{x}10^{-8}$ M

- Considering K_w and K_a, I calculate:

  $[H_3O^+] = 1.988\ \text{x}10^{-7}$ M

A significant difference!!

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Polyprotic acids have multiple equilibria

Phosphoric acid, H_3PO_4, is **tri**protic, so there are three equilibria to consider:

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Polyprotic acids have multiple equilibria

Phosphoric acid, H_3PO_4, is **tri**protic, so there are three equilibria to consider:

$H_3PO_{4\,(aq)} + H_2O_{(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow PO_4^{3-}{}_{(aq)} + H_3O^+{}_{(aq)}$

Each of which has a separate K_a

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Polyprotic acids have multiple equilibria

Phosphoric acid, H_3PO_4, is **tri**protic, so there are three equilibria to consider:

$H_3PO_{4\,(aq)} + H_2O_{(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$
$K_{a1} = 7.5\times10^{-3}$

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$
$K_{a2} = 6.2\times10^{-8}$

$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow PO_4^{3-}{}_{(aq)} + H_3O^+{}_{(aq)}$
$K_{a3} = 5.8\times10^{-13}$

Each of which has a separate K_a

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When calculating the pH of Polyprotic acids, all equilibria must be considered…even if you consider them just to dismiss them!

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Sample Problem

Calculate the pH of a 0.100 M solution of phosphoric acid.

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Solution

As always, we 1st need a balanced equation. Or, in this case, 3 balanced equations!

$H_3PO_{4\,(aq)} + H_2O_{(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$ $K_{a1} = 7.5\times10^{-3}$

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$ $K_{a2} = 6.2\times10^{-8}$

$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow PO_4^{3-}{}_{(aq)} + H_3O^+{}_{(aq)}$ $K_{a3} = 5.8\times10^{-13}$

3 Equilbria = 3 ICE charts!

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Just take them 1 at a time…

$H_3PO_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

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

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$$K_{a1} = 7.5 \times 10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{(0.100 - x)}$$

Can we assume x<<0.100??
Never hurts to try.

$$7.5 \times 10^{-3} = \frac{(x)(x)}{(0.100 - x)} \approx \frac{x^2}{0.100}$$

$7.5 \times 10^{-4} = x^2$

x=0.0274 which is NOT much less than 0.100

We have to do it the Quadratic Way!

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$$K_{a1} = 7.5 \times 10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{(0.100 - x)}$$

$7.5 \times 10^{-4} - 7.5 \times 10^{-3}\,x = x^2$
$0 = x^2 + 7.5 \times 10^{-3}\,x - 7.5 \times 10^{-4}$

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

$x = \frac{-7.5 \times 10^{-3} \pm \text{SQRT}((7.5 \times 10^{-3})^2 - 4(1)(-7.5 \times 10^{-4}))}{2(1)}$

$x = \frac{-7.5 \times 10^{-3} \pm \text{SQRT}(3.0563 \times 10^{-3})}{2}$

$x = \frac{-7.5 \times 10^{-3} \pm 5.528 \times 10^{-2}}{2}$

$x = 2.39 \times 10^{-2}$ M, -3.14×10^{-2} M

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Finish off the first one…

$H_3PO_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

I	0.100	-	0	0
C	-2.39×10^{-2}	-	$+2.39\times10^{-2}$	$+2.39\times10^{-2}$
E	7.61×10^{-2}	-	2.39×10^{-2}	2.39×10^{-2}

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…and start the second one.

$H_2PO_4^-{}_{(aq)} + H_2O_{\,(l)} \leftrightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

I	2.39×10^{-2}	-	0	2.39×10^{-2}
C	-x	-	+x	+x
E	2.39×10^{-2} - x	-	x	2.39×10^{-2} + x

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$$K_{a2} = 6.2\times10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(x)(0.0239+x)}{(0.0239-x)}$$

Let's try x<<0.0239

$6.2\times10^{-8} = \frac{(x)(0.0239+x)}{(0.0239-x)}$

$\approx \frac{x(0.0239)}{0.0239}$

$6.2\times10^{-8} = x$

$x=6.2\times10^{-8}$ which is much less than 0.0239

YIPEE!

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…and start the second one.

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$

	$H_2PO_4^-$	H_2O	HPO_4^{2-}	H_3O^+
I	$2.39x10^{-2}$	-	0	$2.39x10^{-2}$
C	$-6.2x10^{-8}$	-	$+6.2x10^{-8}$	$+6.2x10^{-8}$
E	$2.39x10^{-2}$	-	$6.2x10^{-8}$	$2.39x10^{-2}$

pH=1.62

The K_{a2}<<K_{a1}, so the 2nd and 3rd equilibria are insignificant!

This isn't always true.