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Acid and Base Equilibria

Advanced Concepts

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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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Some Polyprotic Acids

- H_2SO_4 – sulfuric acid
- H_2SO_3 – sulfurous acid
- H_3PO_4 – phosphoric acid
- $\text{H}_2\text{C}_2\text{O}_4$ – oxalic acid
- H_2S – hydrosulfuric acid
- H_2CO_3 – carbonic acid

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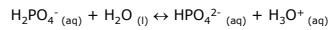
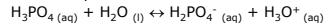
Polyprotic acids have multiple equilibria

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

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Polyprotic acids have multiple equilibria

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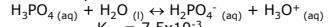


Each of which has a separate K_a

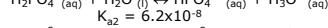
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Polyprotic acids have multiple equilibria

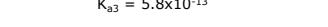
Phosphoric acid, H_3PO_4 , is **triprotic**, so there are three equilibria to consider:



$$K_{a1} = 7.5 \times 10^{-3}$$



$$K_{a2} = 6.2 \times 10^{-8}$$



$$K_{a3} = 5.8 \times 10^{-13}$$

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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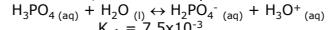
Sample Problem

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

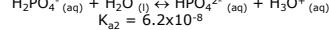
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Solution

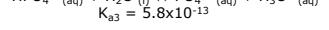
As always, we 1st need a balanced equation. Or, in this case, 3 balanced equations!



$$K_{a1} = 7.5 \times 10^{-3}$$



$$K_{a2} = 6.2 \times 10^{-8}$$



$$K_{a3} = 5.8 \times 10^{-13}$$

3 Equilibria = 3 ICE charts!

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Just take them 1 at a time...



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

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$$K_{a1} = 7.5 \times 10^{-3} = [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4]$$
$$= (x)(x)/(0.100-x)$$

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

$$7.5 \times 10^{-3} = (x)(x)/(0.100-x) \approx x^2/0.100$$
$$7.5 \times 10^{-4} = x^2$$
$$x = 0.0274 \text{ which is NOT much less than 0.100}$$

We have to do it the Quadratic Way!

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$$K_{a1} = 7.5 \times 10^{-3} = [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4]$$
$$= (x)(x)/(0.100-x)$$
$$7.5 \times 10^{-4} - 7.5 \times 10^{-3} x = x^2$$
$$0 = x^2 + 7.5 \times 10^{-3} x - 7.5 \times 10^{-4}$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
$$x = \frac{-7.5 \times 10^{-3} \pm \sqrt{(-7.5 \times 10^{-3})^2 - 4(1)(-7.5 \times 10^{-4})}}{2(1)}$$
$$x = \frac{-7.5 \times 10^{-3} \pm \sqrt{3.0563 \times 10^{-3}}}{2}$$
$$x = \frac{-7.5 \times 10^{-3} \pm 5.528 \times 10^{-2}}{2}$$
$$x = 2.39 \times 10^{-2} \text{ M}$$

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Finish off the first one...

| $\text{H}_3\text{PO}_4 \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \leftrightarrow \text{H}_2\text{PO}_4^- \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)}$ | | | |
|--|---|------------------------|------------------------|
| I | C | E | |
| 0.100 | - | 0 | 0 |
| -2.39×10^{-2} | - | $+2.39 \times 10^{-2}$ | $+2.39 \times 10^{-2}$ |
| 7.61×10^{-2} | - | 2.39×10^{-2} | 2.39×10^{-2} |

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...and start the second one.

| $\text{H}_2\text{PO}_4^- \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \leftrightarrow \text{HPO}_4^{2-} \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)}$ | | | |
|--|---|------|---------------------------|
| I | C | E | |
| 2.39×10^{-2} | - | 0 | 2.39×10^{-2} |
| $-x$ | - | $+x$ | $+x$ |
| $2.39 \times 10^{-2} - x$ | - | x | $2.39 \times 10^{-2} + x$ |

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$$K_{a2} = 6.2 \times 10^{-8} = [\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$$

$$= (x)(0.0239+x)/(0.0239-x)$$

Let's try $x << 0.0239$

$$6.2 \times 10^{-8} = (x)(0.0239+x)/(0.0239-x)$$

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

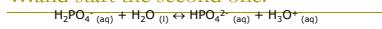
$$6.2 \times 10^{-8} = x$$

$x = 6.2 \times 10^{-8}$ which is much less than 0.0239

YIPEE!

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...and start the second one.



| | | | | |
|---|-----------------------|---|-----------------------|-----------------------|
| I | 2.39×10^{-2} | - | 0 | 2.39×10^{-2} |
| C | -6.2×10^{-8} | - | $+6.2 \times 10^{-8}$ | $+6.2 \times 10^{-8}$ |
| E | 2.39×10^{-2} | - | 6.2×10^{-8} | 2.39×10^{-2} |

The $K_{a2} < K_{a1}$, so the 2nd and 3rd equilibria are insignificant!
This isn't always true. Let's try another example.

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Clicker Question

What is the pH of 0.0100 M H₂SO₄?

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

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

- A. 2.00
- B. 1.70
- C. 1.85
- D. 1.50

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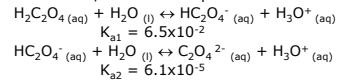
Sample Problem

Calculate the pH of a 1×10^{-3} M solution of oxalic acid.

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Solution

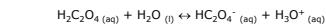
As always, we 1st need a balanced equation. Or, in this case, 2 balanced equations!



2 Equilibria = 2 ICE charts!

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Just take them 1 at a time...



| | 1x10 ⁻³ | - | 0 | 0 |
|---|--------------------|---|----|----|
| I | -x | - | +x | +x |
| C | 1x10 ⁻³ | - | x | x |
| E | -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 $x \ll 1 \times 10^{-3}$

$$6.5 \times 10^{-2} = \frac{(x)(x)}{1 \times 10^{-3} - x} \approx \frac{x^2}{1 \times 10^{-3}}$$
$$6.5 \times 10^{-5} = x^2$$
$$x = 8.06 \times 10^{-3} \text{ which is NOT much less than } 1 \times 10^{-3}$$

We have to do it the Quadratic Way!

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

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

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

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

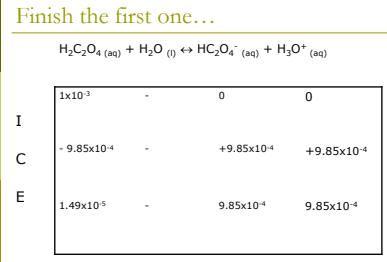
$$x = \frac{-6.5 \times 10^{-2} \pm \sqrt{(6.5 \times 10^{-2})^2 - 4(1)(-6.5 \times 10^{-5})}}{2(1)}$$

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

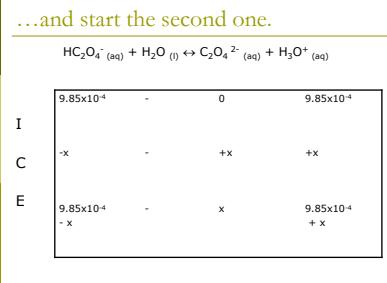
$$x = \frac{-6.5 \times 10^{-2} \pm 6.697 \times 10^{-2}}{2}$$

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

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$$K_{a2} = 6.1 \times 10^{-5} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

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

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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$$K_{a2} = 6.1 \times 10^{-5} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

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

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

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

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

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

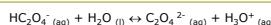
$$x = \frac{-1.046 \times 10^{-3} \pm \sqrt{1.334 \times 10^{-6}}}{2}$$

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

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

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Finishing up...



| | | | | |
|---|------------------------|---|------------------------|------------------------|
| 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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Clicker Question

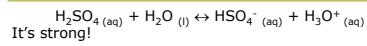
What is the pH of 1×10^{-8} M H_2SO_4 ?

$$K_{a1} = \text{infinite}$$
$$K_{a2} = 1.0 \times 10^{-2}$$

- A. 8.00
- B. 7.70
- C. 5.85
- D. 6.95
- E. 6.70

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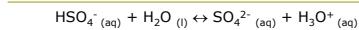
Just take them 1 at a time...



| | | | | |
|---|--------------------|---|--------------------|--------------------|
| 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 $x << 0.100$?
Never hurts to try.

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

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

We have to do it the Quadratic Way!

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

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

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

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

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

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

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

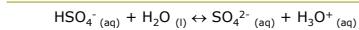
$$x = \frac{-1.000001 \times 10^{-2} \pm 1.000003 \times 10^{-2}}{2}$$

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

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

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Finish off the 2nd one!



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

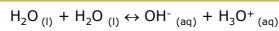
| | | | | |
|--|------------------------|---|--------------------|--------------------|
| | $1 \times 10^{-8} - x$ | - | 1×10^{-8} | 2×10^{-8} |
|--|------------------------|---|--------------------|--------------------|

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

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VERY dilute acid – can't ignore K_w



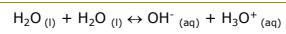
| | | | |
|---|---|------|------------------------|
| I | - | 0 | 2×10^{-8} |
| C | - | $+x$ | $+x$ |
| E | - | x | $2 \times 10^{-8} + x$ |

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$$\begin{aligned}K_w &= 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] \\&\quad (2.0 \times 10^{-8} + x)(x) = \\1.0 \times 10^{-14} &= 2.0 \times 10^{-8}x + x^2 \\0 &= x^2 + 2.0 \times 10^{-8}x - 1.0 \times 10^{-14} \\x &= -\frac{b}{2a} \pm \sqrt{\frac{b^2 - 4ac}{2a}} \\x &= -\frac{2.0 \times 10^{-8}}{2} \pm \sqrt{\frac{(2.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}{2}} \\x &= -\frac{2.0 \times 10^{-8}}{2} \pm \sqrt{4.04 \times 10^{-14}} \\x &= -\frac{2.0 \times 10^{-8}}{2} \pm 2.00998 \times 10^{-7} \\x &= \frac{1.809975 \times 10^{-8}}{2} \\x &= 9.04988 \times 10^{-9} = 9.05 \times 10^{-9}\end{aligned}$$

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Finish off K_w



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

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

$$pH = 6.96$$
