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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
- $H_2C_2O_4$ – 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 **tri**protic, so there are three equilibria to consider:

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## Polyprotic acids have multiple equilibria

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

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

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

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…

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

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

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

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

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

We have to do it the Quadratic Way!

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$K_{a1} = 7.5\text{x}10^{-3} = [H_3O^+][H_2PO_4^-]/[H_3PO_4]$
$= (x)(x)/(0.100-x)$
$7.5\text{x}10^{-4} - 7.5\text{x}10^{-3}\,x = x^2$
$0 = x^2 + 7.5\text{x}10^{-3}\,x - 7.5\text{x}10^{-4}$

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

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

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

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

$x = 2.39\text{x}10^{-2}$ 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 | $-2.39\times10^{-2}$ | - | $+2.39\times10^{-2}$ | $+2.39\times10^{-2}$ |
| E | $7.61\times10^{-2}$ | - | $2.39\times10^{-2}$ | $2.39\times10^{-2}$ |

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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 | $2.39\times10^{-2}$ | - | 0 | $2.39\times10^{-2}$ |
| C | -x | - | +x | +x |
| E | $2.39\times10^{-2}$ - x | - | x | $2.39\times10^{-2}$ + x |

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

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.

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

| | | | | |
|---|---|---|---|---|
| I | $2.39x10^{-2}$ | - | 0 | $2.39x10^{-2}$ |
| C | $-6.2x10^{-8}$ | - | $+6.2x10^{-8}$ | $+6.2x10^{-8}$ |
| E | $2.39x10^{-2}$ | - | $6.2x10^{-8}$ | $2.39x10^{-2}$ |

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 $H_2SO_4$?
$K_{a1}$ = infinite
$K_{a2} = 1.0x10^{-2}$

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

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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 Equilbria = 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 $x<<1x10^{-3}$

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

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

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

We have to do it the Quadratic Way!

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

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

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

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

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

$x = \frac{-6.5\text{x}10^{-2} \pm \text{SQRT}(4.485\text{x}10^{-3})}{2}$

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

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

## Slide 23

### Finish the first one…

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

| | | | | |
|---|---|---|---|---|
| I | $1\text{x}10^{-3}$ | - | 0 | 0 |
| C | $-9.85\text{x}10^{-4}$ | - | $+9.85\text{x}10^{-4}$ | $+9.85\text{x}10^{-4}$ |
| E | $1.49\text{x}10^{-5}$ | - | $9.85\text{x}10^{-4}$ | $9.85\text{x}10^{-4}$ |

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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 | $9.85\text{x}10^{-4}$ | - | 0 | $9.85\text{x}10^{-4}$ |
| C | -x | - | +x | +x |
| E | $9.85\text{x}10^{-4}$ - x | - | x | $9.85\text{x}10^{-4}$ + 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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$$K_{a2} = 6.1x10-5 = \frac{[H_3O+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

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

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

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

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

x = $\frac{-1.046x10^{-3} +/- SQRT((1.046x10^{-3})^2-4(1)(-6.0085x10^{-8}))}{2(1)}$

x = $\frac{-1.046x10^{-3} +/- SQRT(1.334x10^{-6})}{2}$

x = $\frac{-1.046x10^{-3} +/- 1.155x10^{-3}}{2}$

x = $5.46x10^{-5}$ M

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### Finishing up…

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

| | | | | |
|---|---|---|---|---|
| I | $9.85x10^{-4}$ | - | 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.

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## Clicker Question

What is the pH of $1x10^{-8}$ M $H_2SO_4$?
$K_{a1}$ = infinite
$K_{a2}$ = $1.0x10^{-2}$

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…

$H_2SO_{4\ (aq)} + H_2O_{\ (l)} \leftrightarrow HSO_4^-{}_{\ (aq)} + H_3O^+{}_{\ (aq)}$
It's strong!

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

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## 2nd one starts where 1st one ends!

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

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

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$K_{a2} = 1.0x10^{-2} = \frac{[H_2O^+][SO_4^{2-}]}{[HSO_4^-]}$

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

Can we assume x<<0.100??
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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## AND START THE $3^{RD}$ 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