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Acid/Base Properties of Salts

Hiding in plain sight

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Recognizing Bases

Sometimes it seems that all acids and bases are labeled with H^+ or OH^-

Acids do have an H^+

But a base is ANYTHING that can accept a proton – it doesn't have to have an OH-. Anything with a negative charge or just non-bonding electrons (N, O, P) can act as a base.

The salt formed by the dissociation of an acid is the "conjugate base" of the acid. This must mean that the salt is a base, whether it has an OH- or not.

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Pick a salt, any salt

- How about ammonium acetate, NH_4OAc? An excellent choice.
  - SALT = IONIC
- Ammonium acetate is an ionic solid.
- Ionic solids **dissociate** in aqueous solution
- Aqueous NH_4OAc will exist as anions and cations.

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The MOST important thing about salts!

$NH_4OAc_{(aq)} \rightarrow NH_4^+{}_{(aq)} + OAc^-{}_{(aq)}$

So what can we say about NH_4^+ and OAc^- in aqueous solution?

We need to think "backwards". How did NH_4OAc get the NH_4^+ in the first place? (Or, more accurately, what is one way it could have gotten it?)

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Salts are products of acid/base reactions

You might recall that the reaction of an acid and a base yields a salt and water:

$NH_4OH + HOAc \rightarrow H_2O + NH_4OAc$

$NH_3 + HOAc \rightarrow NH_4OAc$

These are the same reaction!

Hey, look! It's our salt!

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These two reactions are identical

$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$ $K_b(NH_3)$

$NH_3 + H_2O = NH_4OH$

$NH_4OH + HOAc \rightarrow H_2O + NH_4OAc$

$NH_3 + H_2O + HOAc \rightarrow H_2O + NH_4OAc$

$NH_3 + HOAc \rightarrow NH_4OAc$

NH_4OH is just another way to write aqueous NH_3

This is why I often say that bases don't need to have an OH- because they borrow one from water.

The whole acid + base = salt + water is a slight exaggeration. Sometimes you borrow OH- from water!

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A more detailed reaction

Let's stick to the more plain:

$NH_3(aq) + HOAc \rightarrow NH_4OAc(aq)$

But what are $NH_{3\,(aq)}$ and $HOAc_{\,(aq)}$?

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Acid (and Base) Dissociation Reactions

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

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

Hey, look! It's pieces of our salt!

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Putting it all together…

$NH_4OAc_{(aq)} \rightarrow NH_4^+{}_{(aq)} + OAc^-{}_{(aq)}$

$NH_{3(aq)}$	$+ H_2O_{(l)} \leftrightarrow$	$NH_4^+{}_{(aq)}$	+	$OH^-{}_{(aq)}$	K_b
Base	acid	conjugate acid		conjugate base	
$HOAc_{(aq)}$	$+ H_2O_{(l)} \leftrightarrow$	$H_3O^+{}_{(aq)}$	+	$OAc^-{}_{(aq)}$	K_a
Acid	base	conjugate acid		conjugate base	

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In short…

We have the conjugate acid (NH_4^+) of a base (NH_3 or NH_4OH), and the conjugate base (OAc^-) of an acid (HOAc).

THIS IS A GENERAL RULE!

All salts are the combination of a (conjugate) acid and a (conjugate) base!

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An acid is an acid.

A base is a base.

"Conjugate" or not.

And water is both!

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K_b becomes K_a as K_a becomes K_b

Just because you're a "conjugate acid" doesn't mean you're not an acid!

NH_4^+ (aq) + H_2O (l) ↔ NH_3 (aq) + H_3O^+ (aq)
$K_a=K_w/K_b$

$OAc^-_{(aq)}$ + $H_2O_{(l)}$ ↔ $OH^-_{(aq)}$ + HOAc $_{(aq)}$
$K_b=K_w/K_a$

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$NH_{3\ (aq)} + H_2O_{(l)} \leftrightarrow OH^-_{\ (aq)} + NH_4^+{}_{(aq)}$ K_b=1.76x10^{-5}

NH_4^+ (aq) + H_2O (l) ↔ NH_3 (aq) + H_3O^+ (aq)

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.76\times10^{-5}} = 5.68\times10^{-10}$$

$HOAc_{\ (aq)} + H_2O_{(l)} \leftrightarrow H_3O^+{}_{(aq)} + OAc^-{}_{(aq)}$ K_a =1.8x10^{-5}

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

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

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Important Points

- All acids/bases are conjugate pairs of compounds. It's an equilibrium, they go both ways.
- Conjugate reaction pairs have K_axK_b=K_w
- For this particular salt it is approximately equally "acidic" and "basic" and so it ends up being neutral. This is not usually the case. The K_a and K_b just happen to be really close in this case.
- In general, you'd need to solve both ICE charts to get the pH…but not always.

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Pick a new salt, any salt

- How about sodium acetate, NaOAc? An excellent choice.
- Sodium acetate is an ionic solid.
- Ionic solids dissociate in aqueous solution
- Aqueous NaOAc will exist as anions and cations.

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Salts dissociate in water

NaOAc (aq) = Na^+ (aq) + OAc^- (aq)

It's a little less obvious what's going on here. But ALL SALTS are made up of an acid (cation) part and a base (anion) part.

It's just that Na^+ doesn't look like much of an acid. But again, that's because it borrows from water!

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Acid (and Base) Dissociation Reactions

$NaOH_{(aq)} + H_2O_{(l)} \leftrightarrow H\text{-}OH_{(l)} + OH^-_{(aq)} + Na^+_{(aq)}$ K_b

Or: $NaOH \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

$OH^-_{(aq)} + H_2O_{(l)} \leftrightarrow H\text{-}OH_{(l)} + OH^-_{(aq)}$ K_b

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

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Putting it all together…

$NaOAc_{(aq)} \rightarrow Na^+_{(aq)} + OAc^-_{(aq)}$

$NaOH_{(aq)} + H_2O_{(l)} \leftrightarrow OH^-_{(aq)} + Na^+_{(aq)} + H\text{-}OH_{(l)}$

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

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Putting it all together…

$NaOAc_{(aq)} \rightarrow Na^+_{(aq)} + OAc^-_{(aq)}$

$NaOH_{(aq)} + H_2O_{(l)} \leftrightarrow OH^-_{(aq)} + Na^+_{(aq)} + H\text{-}OH_{(l)}$

Base acid conjugate base conjugate acid

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

Base acid conjugate acid conjugate base

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In short…

We have the conjugate acid (Na^+) of a base (NaOH), and the conjugate base (OAc^-) of an acid (HOAc).

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K_b becomes K_a as K_a becomes K_b

$NaOAc_{(aq)} \rightarrow Na^+_{(aq)} + OAc^-_{(aq)}$

$Na^+_{(aq)} + 2\ H_2O_{(l)} \leftrightarrow NaOH_{(aq)} + H_3O^+_{(aq)}$

(or, if you prefer)

$Na^+_{(aq)} + H_2O_{(l)} \leftrightarrow NaOH_{(aq)} + H^+_{(aq)}$ $K_a=K_w/K_b$

$OAc^-_{(aq)} + H_2O_{(l)} \leftrightarrow OH^-_{(aq)} + HOAc_{(aq)}$ $K_b=K_w/K_a$

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But one is strong and the other weak.

$NaOH_{(aq)} + H_2O_{(l)} \leftrightarrow H\text{-}OH_{(l)} + OH^-_{(aq)} + Na^+_{(aq)}$ $K_b=\infty$

$Na^+_{(aq)} + H_2O_{(l)} \leftrightarrow NaOH_{(aq)} + H^+_{(aq)}$ $K_a=K_w/K_b = 0$

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$ $K_a = 1.8x10^{-5}$

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

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

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Net Result

NaOAc gives rise to a single equilibrium reaction that must be considered:

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

$K_b=5.56x10^{-10}$

The salt is a base!!!!

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What is the pH of a 0.100 M NaOAc solution?

We need to recognize this as a salt solution.

As soon as we recognize it as a salt, it has an acid half and a base half.

In this case, we can ignore the Na^+ because it comes from a strong base (it ain't going back!) and so it is only the OAc^- that matters.

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What is the pH of a 0.100 M NaOAc solution?

It's a base equilibrium so…THERE'S 3 PARTS!

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

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10} = \frac{[OH-][HOAc]}{[OAc-]}$$

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ICE-ICE-BABY-ICE-ICE

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

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

$$5.56\times10^{-10} = \frac{[OH-][HOAc]}{[OAc-]} = \frac{(x)(x)}{0.100-x}$$

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How do we solve it?

$$5.56 \times 10^{-10} = \frac{(x)(x)}{0.100 - x}$$

Assume x<<0.100

$$5.56 \times 10^{-10} = \frac{(x)(x)}{0.100}$$

$$5.56 \times 10^{-11} = x^2$$
$$x = 7.46 \times 10^{-6}$$

Pretty darn good assumption!

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ICE-ICE-BABY-ICE-ICE

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

I	0.100 M	-	0	0
C	-x	-	+x	+x
E	0.0999925	-	7.46×10^{-6}	7.46×10^{-6}

$$pOH = -\log(7.46 \times 10^{-6}) = 5.12$$

$$pH = 14 - pOH = 14 - 5.12 = 8.88$$

That's a pretty basic little solution we have!

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Sample Problem

What is the pH of a solution of 0.0707 M potassium phosphate in water?

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1st we need…

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…a balanced equation

$K_3PO_4 {}_{(aq)} \rightarrow 3\ K^+{}_{(aq)} + PO_4^{3-}{}_{(aq)}$

Now, potassium is the conjugate acid of KOH – a strong base.

PO_4^{3-} is the conjugate base of hydrogen phosphate, HPO_4^{2-} (which is the conjugate base of $H_2PO_4^-$, which is the conjugate base of H_3PO_4)

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So, there may be 3 equilibria to consider

$H_3PO_4 {}_{(aq)} + H_2O {}_{(l)} \leftrightarrow H_2PO_4^- {}_{(aq)} + H_3O^+ {}_{(aq)}$

$K_{a1} = 7.5x10^{-3}$

$H_2PO_4^- {}_{(aq)} + H_2O {}_{(l)} \leftrightarrow HPO_4^{2-} {}_{(aq)} + H_3O^+ {}_{(aq)}$

$K_{a2} = 6.2x10^{-8}$

$HPO_4^{2-} {}_{(aq)} + H_2O {}_{(l)} \leftrightarrow PO_4^{3-} {}_{(aq)} + H_3O^+ {}_{(aq)}$

$K_{a3} = 5.8x10^{-13}$

But, of course, we need the reverse reactions

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So, there may be 3 equilibria to consider

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3PO_4{}_{(aq)} + OH^-{}_{(aq)}$

$K_{b1} = \frac{K_w}{K_{a1}} = \frac{1\times10^{-14}}{7.5\times10^{-3}} = 1.33 \times 10^{-12}$

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

$K_{b2} = \frac{K_w}{K_{a2}} = \frac{1\times10^{-14}}{6.2\times10^{-8}} = 1.61 \times 10^{-7}$

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

$K_{b3} = \frac{K_w}{K_{a3}} = \frac{1\times10^{-14}}{5.8\times10^{-13}} = 1.72 \times 10^{-2}$

This is the thing I have!

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Just take them 1 at a time…

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

I	0.0707 M	-	0	0
C	-x	-	+x	+x
E	0.0707 -x	-	x	x

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$$K_{b3} = 1.72 \times 10^{-2} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]} = \frac{(x)(x)}{(0.0707 - x)}$$

Try x<<0.0707

$$1.72 \times 10^{-2} = \frac{(x)(x)}{(0.0707 - x)} \approx \frac{x^2}{0.0707}$$

$1.22\times10^{-3} = x^2$

x=0.0349 which is NOT much less than 0.0707

We have to do it the Quadratic Way!

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$$K_{b3} = 1.72 \times 10^{-2} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]} = \frac{(x)(x)}{(0.0707 - x)}$$

$1.216x10^{-3} - 1.72x10^{-2}\,x = x^2$

$0 = x^2 + 1.72x10^{-2}\,x - 1.216x10^{-3}$

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

$x = \frac{-1.72x10^{-2} +/- SQRT((1.72x10^{-2})^2-4(1)(-1.216x10^{-3}))}{2(1)}$

$x = \frac{-1.72x10^{-2} +/- SQRT(5.16x10^{-3})}{2}$

$x = \frac{-1.72x10^{-2} +/- 7.18x10^{-2}}{2}$

$x = 2.73x10^{-2}$ M

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The 1st equilibrium…

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

I	0.0707 M	-	0	0
C	$-2.73x10^{-2}$	-	$+2.73x10^{-2}$	$+2.73x10^{-2}$
E	0.0434	-	$2.73x10^{-2}$	$2.73x10^{-2}$

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…leads to the second

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

I	$2.73x10^{-2}$ M	-	0	$2.73x10^{-2}$
C	- x	-	+x	+x
E	$2.73x10^{-2}$ -x	-	x	$2.73x10^{-2}$ + x

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$$K_{b2} = 1.61 \times 10^{-7} = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]}$$

$$K_{b2} = 1.61 \times 10^{-7} = \frac{(x)(x + 2.73 \times 10^{-2})}{(2.73 \times 10^{-2} - x)}$$

Try x<<0.0273

$$1.61 \times 10^{-7} = \frac{(x)(x + 2.73 \times 10^{-2})}{(2.73 \times 10^{-2} - x)} \approx \frac{(x)(2.73 \times 10^{-2})}{2.73 \times 10^{-2}}$$

$1.61 \times 10^{-7} \approx x$

$1.61 \times 10^{-7} = x$

This is not only small relative to the 0.0273, it is just completely insignificant!

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…leads to the second

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

I	2.73×10^{-2} M	-	0	2.73×10^{-2}
C	$- 1.61 \times 10^{-7}$	-	$+1.61 \times 10^{-7}$	$+1.61 \times 10^{-7}$
E	2.73×10^{-2}	-	1.61×10^{-7}	2.73×10^{-2}

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If we needed a 3rd chart…it starts there:

$H_2PO^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3PO_4{}_{(aq)} + OH^-{}_{(aq)}$

I	1.61×10^{-7} M	-	0	2.73×10^{-2}
C	- x	-	+x	+x
E	1.61×10^{-7} -x	-	x	2.73×10^{-2}+x

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But if the 2nd one didn't matter…

…the 3rd one matters even less…

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow H_3PO_4{}_{(aq)} + OH^-{}_{(aq)}$

$K_{b1} = \frac{K_w}{K_{a1}} = \frac{1\times10^{-14}}{7.5\times10^{-3}} = 1.33 \times 10^{-12}$

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

$K_{b2} = \frac{K_w}{K_{a2}} = \frac{1\times10^{-14}}{6.2\times10^{-8}} = 1.61 \times 10^{-7}$

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

$K_{b3} = \frac{K_w}{K_{a3}} = \frac{1\times10^{-14}}{5.8\times10^{-13}} = 1.72 \times 10^{-2}$

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Calculating the pH

The result of our 2nd ICE chart is that:

$[OH-]= 2.73\text{x}10^{-2}$

What do we do with this number?

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Calculating the pH

The result of our ICE chart (1st or 2nd) is that:

$[OH-]= 2.73\text{x}10^{-2}$

What do we do with this number?

1. To calculate the pH directly, we need $[H_3O^+]$
2. We can calculate the pOH, and then get the PH from that.

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Calculating the pH from $[OH^-]$

1. To calculate the pH directly, we need $[H_3O^+]$
   Recall that $K_w = 1x10^{-14} = [H_3O^+][OH^-]$
   $1x10^{-14} = [H_3O^+][2.73x10^{-2}]$
   $[H_3O^+] = 3.66x10^{-13}$
   $pH = - \log ([H_3O^+])$
   $pH = - \log (3.66x10^{-13})$
   $pH = 12.44$
2. We can calculate the pOH, and then get the PH from that.
   Recall that pOH + pH = 14
   $pOH = - \log ([OH^-]) = - \log (2.73x10^{-2}) = 1.56$
   pH = 14 – pOH = 14 – 1.56 = 12.44

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A few concluding observations

- The pH ended up being 12.44, nicely basic as we expected.
- This is nothing new: K IS K IS K IS K
- While it is a multiple equilibrium problem, as we saw for the polyprotic acids, if there is a significant difference in K, not all of the equilibria will contribute meaningfully.

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For all salts IN WATER:

1. Separate into ions.
2. The cation is the conjugate acid.
   The anion is the conjugate base.
3. For the cation: either add OH- or, if there is one, remove the H^+ to see what base "it came from".
4. For the anion: add an H^+ to see what acid "it came from".
5. Look up the K_a and K_b of the "parent" acid/base.
6. Ignore strong acids and bases!

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Consider 0.100 M NaCl

Is it acid, basic or neutral?
Separate into ions.
$NaCl=Na^{+} + Cl^{-}$
The cation (Na+) is the conjugate acid.
The anion (Cl-) is the conjugate base.
A. Acid
B. Base
C. Neutral
D. Both an acid and a base
E. Your mother

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Consider 0.100 M NaCl

Is it acid, basic or neutral?

- For the cation: either add OH- or, if there is one, remove the H^{+} to see what base "it came from".

$Na^{+} + OH^{-} = NaOH$
For the anion: add an H^{+} to see what acid "it came from".
$Cl^{-} + H^{+} = HCl$

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Consider 0.100 M NaCl

Is it acid, basic or neutral?
Look up the K_a and K_b of the "parent" acid/base.
NaOH – strong base
HCl – strong acid

We can ignore both of them so the salt is neutral!

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Consider 0.100 M NH_4Cl

Is it acid, basic or neutral?
Separate into ions.
$NH_4Cl = NH_4^+ + Cl^-$
The cation (NH_4+) is the conjugate acid.
The anion (Cl-) is the conjugate base.
A. Acid
B. Neutral
C. Basic
D. None of the Above
E. All of the above

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Consider 0.100 M NH_4Cl

Is it acid, basic or neutral?
- For the cation: either add OH- or, if there is one, remove the H^+ to see what base "it came from".

$NH_4^+ - H^+ = NH_3$
For the anion: add an H^+ to see what acid "it came from".
$Cl^- + H^+ = HCl$

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Consider 0.100 M NH_4Cl

Is it acid, basic or neutral?
Look up the K_a and K_b of the "parent" acid/base.
NH_3 – $K_b = 1.76 \times 10^{-5}$
HCl – strong acid

We ignore the HCl. The NH_3 counts.

Clickers!

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What is the pH of 0.100 M NH_4Cl

A. 2.88
B. 11.12
C. 4.75
D. 5.12
E. 8.88
F. 1.00
G. 0.100
H. 2.00
I. None of the above