Tutorial 4: K_a & K_b for Weak acids and Bases

Reminder: pH of SA's

$[H_3O^+]$=[acid] ***strong*** means 100% ionized

so, to find pH of 0.100 M HCl

$[H_3O^+] = 0.100$ M
pH = 1.000

For weak acids $[H_3O^+] << [acid]$

Eg.) What is pH of 0.10 M HF?

Look at equilibrium for **Weak** Acid HF

$$HF_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + F^-_{(aq)}$$

Dissolved but not ionized

Pure liquid not included in Keq expression.

$$Keq = \frac{[H_3O^+][F^-]}{[HF]}$$

for WA's Keq is called K_a (***acid*** ionization constant)

- see acid table for list of Ka's.

higher Ka → stronger acid
lower Ka → weaker acid

For SA's (eg. HCl) $Ka = \frac{[H_3O^+][Cl^-]}{[HCl]}$ = called "very large!"

Essentially **zero** molecular HCl

-Discuss Relative Strengths of Oxyacids

Calculations Using Ka (*Used for Weak Acids*)

$[H_3O^+]$ from Ka (pH from Ka)

1. $[H_3O^+]$ from Ka and Original concentration (Co)

eg.) Find the $[H_3O^+]$ in 0.10 M HF

WA

1. Write out equilibrium equation for *ionization*

$$HF + H_2O \leftrightarrows H_3O^+ + F^-$$

2. Ice table

	HF	+ H_2O	⇆ H_3O^+	+ F^-
[I]	0.10		0	0
[C]	-x		+x	+x
[E]	0.10 –x		x	x

3. Ka expression: $Ka = \frac{[H_3O^+][F^-]}{[HF]}$

$$Ka = \frac{(x)\,(x)}{0.10 - x}$$

To avoid quadratic assume x is insignificant compared to 0.10 This can be confirmed later.

In Chem. 12 with weak acids, always use this assumption - Make sure you state it!

4. Substitute $Ka = \frac{x^2}{0.10}$

(Assume 0.10 – x ≅ 0.10)

You **must** state this assumption here!

5. Solve for x ($[H_3O^+]$)

$Ka = \frac{x^2}{0.100}$ So $x^2 = 0.10\ Ka$

$$[H_3O^+] = x = \sqrt{0.10\ Ka}$$

$$= \sqrt{0.10\ (3.5 \times 10^{-4})}$$

Ka from Acid Table

$[H_3O^+] = 5.9 \times 10^{-3}$ M

~ Check assumption (*we see that this is quite small compared to 0.10*)

NOTE: Ions which act as acids can come from compounds.

Eg.) See table ~ ammonium ion NH_4^+
- can be found in NH_4NO_3, NH_4Cl, NH_4Br, etc….
ferric (hexaaquoiron) Fe^{3+} ($Fe(H_2O)_6^{3+}$) could be found in $Fe(H_2O)_6Br_3$ (also called $FeBr_3$)
or $Fe(H_2O)_6(NO_3)_3$ (also called $Fe(NO_3)_3$)

Aluminum (hexaaquoaluminum) Al^{3+} ($Al(H_2O)_6^{3+}$) could be found in $Al(H_2O)_6Cl_3$ (also called $AlCl_3$)

More Ka Calculations:

NOTE: the pH is to 3 SD's so your final answer cannot have more than 3 SD's.

Ka from pH

Eg.) a 0.350 M Solution of the weak acid HA has a pH of 1.620. Find the Ka of HA.

1. First convert pH to $[H_3O^+]$

$[H_3O^+]$ = antilog (-pH)
= antilog (-1.620)
$[H_3O^+] = 2.399 \times 10^{-2}$ M

This is the $[H_3O^+]$ at equilibrium

2. Write out equilibrium equation for ionization. Make an ICE table:

	HA	+ H_2O	⇆ H_3O^+	+ A^-
[I]	0.350		0	0
[C]				
[E]			2.399×10^{-2}	

Now, you can see that the change in concentration [C] of $[H_3O^+]$ is + 2.399×10^{-2} M and using the mole ratios (mole bridges) in the balanced equation, you can figure out the [C]'s for the A^- and the HA:

	-2.399×10^{-2}M		$+ 2.399 \times 10^{-2}$M	$+ 2.399 \times 10^{-2}$M
	HA	+ H_2O ⇆	H_3O^+	+ A^-
[I]	0.350		0	0
[C]	$- 2.399 \times 10^{-2}$		$+ 2.399 \times 10^{-2}$	$+ 2.399 \times 10^{-2}$
[E]			2.399×10^{-2}	

Now, we can figure out the equilibrium concentrations of HA and A^-. There are no "x"s in the table so we don't need to make any assumptions. It is best to use your calculator to figure out the equilibrium [HA], because the [C] may or MAY NOT be insignificant. Using a calculator $0.350 - 2.399 \times 10^{-2} = 0.32601$. Don't round it off too much here. I would keep it in a memory in my calculator. BUT BECAUSE THE "0.350" IS 3 DECIMAL PLACES AND YOU ARE SUBTRACTING, THE [E] OF "HA" CANNOT HAVE MORE THAN 3 DECIMAL PLACES (although you should use 0.32601 in your calculator) JUST REMEMBER THAT IN THE NEXT CALCULATION, THE 3 DECIMAL PLACES IN THE ICE TABLE TRANSLATES TO 3 SD'S, SO YOUR FINAL ANSWER CANNOT HAVE MORE THAN 3 SD'S.

	-2.399×10^{-2}M		$+ 2.399 \times 10^{-2}$M	$+ 2.399 \times 10^{-2}$M
	HA	+ H_2O ⇆	H_3O^+	+ A^-
[I]	0.350		0	0
[C]	$- 2.399 \times 10^{-2}$		$+ 2.399 \times 10^{-2}$	$+ 2.399 \times 10^{-2}$
[E]	*0.326*		*2.399×10^{-2}*	*2.399×10^{-2}*

3. Write Ka expression & substitute values.

$$Ka = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(2.399 \times 10^{-2})^2}{0.326} = 1.7653 \times 10^{-3}$$ and expressing in 3SD's, the answer is:

Ka = 1.77×10^{-3}

To Calculate Co (conc. of acid needed) form pH & Ka

Eg. Find the concentration of HCOOH needed to form a solution with pH = 2.69

1. First change pH to $[H_3O^+]$

$[H_3O^+]$ = antilog (-pH)

= antilog (-2.69)

$[H_3O^+] = 2.0417 \times 10^{-3}$ M (notice that the given pH limits us to 2SD's, but keep more in your calculations.)

2. Write out ionization equilibrium with an ICE TABLE. You can insert 2.0417×10^{-3} for equilibrium $[H_3O^+]$. And since our **unknown** is the initial [HCOOH], we put in an "C_o" for the [I] of HCOOH:

	HCOOH	+ H_2O ⇆	H_3O^+	+ $HCOO^-$
[I]	C_o		0	0
[C]				
[E]			2.0417×10^{-3}	

Now we can see that the change in concentration [C] of [H_3O^+] is " + 2.0417 x 10^{-3} " and the [C] of $HCOO^-$ will be the same. The [C] of HCOOH will be " - 2.0417 x 10^{-3} "

	$HCOOH$ +	H_2O ⇆	H_3O^+ +	$HCOO^-$
[I]	C_o		0	0
[C]	*- 2.0417 x 10^{-3}*		*+ 2.0417 x 10^{-3}*	*+ 2.0417 x 10^{-3}*
[E]			2.0417 x 10^{-3}	

We can now calculate the equilibrium concentrations [E] of HCOOH and $HCOO^-$.

	$HCOOH$ +	H_2O ⇆	H_3O^+ +	$HCOO^-$
[I]	C_o		0	0
[C]	- 2.0417 x 10^{-3}		+ 2.0417 x 10^{-3}	+ 2.0417 x 10^{-3}
[E]	C_o *- 2.0417 x 10^{-3}*		*2.0417 x 10^{-3}*	*2.0417 x 10^{-3}*

The next step will be to write the K_a expression and substitute the equilibrium concentrations in:

3. Write Ka expression. Substitute equilibrium concentrations in. Find Ka for HCOOH on the acid table:

$$Ka = \frac{[H_3O^+]\,[HCOO^-]}{[\,HCOOH]}$$

Find Ka on Acid Table

$$1.8 \times 10^{-4} = \frac{(2.0417 \times 10^{-3})^2}{(\,Co - 2.0417 \times 10^{-3})}$$

Now we can solve for Co (the original concentration of the acid):

$$Co - 2.0417 \times 10^{-3} = \frac{(2.0417 \times 10^{-3})^2}{1.8 \times 10^{-4}}$$

$$Co - 2.0417 \times 10^{-3} = 2.3159 \times 10^{-2}$$

$$Co = 2.3159 \times 10^{-2} + 2.0417 \times 10^{-3}$$

$$Co = 2.52 \times 10^{-2}\ M$$

Co = 2.5 x 10^{-2} M or 0.025 M (remember, we are restricted to 2 SD's)

Now For Bases

Base ionization NH_3 → very common weak base. It partially ionizes in water to form NH_4^+ and OH^- :

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

Equilibrium constant – called **base ionization constant** (Kb)

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

Kb expression: $Kb = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$

NOTE: Ions can also act as a weak bases. The reaction of an **ion** with water to form OH^- is called **base hydrolysis**. Equilibrium constant is still called Kb.

Eg.) **Hydrolysis** of CN^-

$$CN^-_{(aq)} + H_2O_{(l)} \leftrightarrows HCN_{(aq)} + OH^-_{(aq)}$$

Already an **ion**

$$Kb = \frac{[HCN][OH^-]}{[CN^-]}$$

Kb expression

Ionization of N_2H_4 (weak base)

$$N_2H_{4\,(aq)} + H_2O_{(l)} \leftrightarrows N_2H_5^+{}_{(aq)} + OH^-_{(aq)}$$

A neutral molecule

$$Kb = \frac{[N_2H_5^+]\,[OH^-]}{[N_2H_4]}$$

Kb expression

How to Find Kb using Acid Table

(not shown directly)

Derivation

- Look at **hydrolysis** of base F^-: $F^- + H_2O \leftrightarrows HF + OH^-$

$$Kb_{\,(F-)} = \frac{[HF]\,[OH^-]}{[F^-]}$$

- Look at **ionization** the weak acid HF: $HF + H_2O \leftrightarrows H_3O^+ + F^-$

$$Ka_{\,(HF)} = \frac{[H_3O^+]\,[F^-]}{[HF]}$$

- **Multiply** $Ka_{[HF]}$ x $Kb_{[F^-]}$

Conj. Acid

Conj. base

$$Ka_{[HF]} \times Kb_{[F^-]} = \frac{[H_3O^+]\,[F^-]}{[HF]} \times \frac{[HF]\,[OH^-]}{[F^-]} = [H_3O^+]\,[OH^-]$$ (*notice that [HF] and [F⁻] will cancel.*)

or $\mathbf{Ka_{(HF)} \times Kb_{(F^-)} = Kw}$

$Ka_{(HF)} \times Kb_{(F^-)} = Kw$

Or $Kb_{(F^-)} = \dfrac{Kw}{Ka_{(HF)}}$

In general:

$$\boxed{\mathbf{Kb_{(weak\ base)} = \frac{Kw}{Ka_{(it's\ conj.\ acid)}}}}$$

Using Acid Table:

1. Find base on ***right*** side (if amphiprotic -locate base on **right** side only)
2. It's conjugate acid will be across from it on the left side.
3. The Ka of it's conjugate acid is on the **far right** of the same line.
4. Use equation: $Kb_{(base)} = \frac{Kw}{Ka(\text{conj. acid})}$

Eg.) Calculate the Kb for HCO_3^- : (find HCO_3^- on **RIGHT** SIDE)

Line: $H_2CO_3 \leftrightarrows H^+ + HCO_3^-$………$4.3 \times 10^{-7}$

It's conj. acid

Base

$Ka_{(\text{it's conj. acid})}$

$$Kb(HCO_3^-) = \frac{Kw}{Ka(H_2CO_3)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Find Kb of SO_3^{2-}

Similarly : If Kb (base) given

$$\boxed{\textbf{Ka (weak acid)} = \frac{\textbf{Kw}}{\textbf{Kb(it's conj. Base)}}}$$

Eg.) The Kb for base B^- is 2.73×10^{-9}
Find the Ka for the acid HB

3 sig. Digs.

$$Ka_{(HB)} = \frac{Kw}{Kb_{(B^-)}} = \frac{1.00 \times 10^{-14}}{2.73 \times 10^{-9}} = \underline{3.66 \times 10^{-6}}$$

NOTES:

- Table only states Ka values. For questions like this Kb will have to be calculated if not given.
- All Ka's on table are 2 SD's—limits any calculation using them to 2 SD's maximum.
- The larger the Kb, the "stronger " the weak base - the more OH^- produced.
- The smaller the Ka of an acid, the larger the Kb of its conjugate Base. (*Weaker acids have stronger conjugate bases*)

Calculations Involving Kb

Given:		Find		or find		or find
[Base] & Kb	→	$[OH^-]$	→	pOH	→	pH

eg.) Find $[OH^-]$ in a 0.20 M solution of KNO_2 (*this is a <u>salt</u>, so it must be dissociated into it's ions first*)

Dissociation of $KNO_2 \rightarrow K^+ + NO_2^-$

Neutral spectator (discard)

Weak base

1. Find Kb of NO_2^-

$$K_b(NO_2^-) = \frac{Kw}{K_a(HNO_2)} = \frac{1.0 \times 10^{-1}}{4.6 \times 10^{-4}}$$

$K_b(NO_2) = 2.174 \times 10^{-11}$

2. Hydrolysis (if ion) or ionization (if molecule) equation followed by an ICE table:

	NO_2^-	$+ H_2O \leftrightarrows$	HNO_2 +	OH^-
[I]	0.20		0	0
[C]				
[E]				

We can let "x" equal the moles/L of NO_2^- which hydrolyze as the reaction reaches equilibrium.
Using the mole ratios in the equation and calculating [E]'s we get:

	NO_2^-	$+ H_2O \leftrightarrows$	HNO_2 +	OH^-
[I]	0.20		0	0
[C]	-x		+x	+x
[E]	**0.20 - x**		**x**	**x**

3. K_b Expression:

$$K_b = \frac{[HNO_2]\,[OH^-]}{[NO_2^-]} \quad \text{at equilibrium}$$

We substitute the [E]'s into the Kb expression

Substitute: $Kb = \frac{[HNO_2]\,[OH^-]}{[NO_2^-]}$ or $Kb = \frac{x^2}{(0.20\ -\ x)}$

Original conc. of NO_2^- (Co)

Assume that $0.20 - x \cong 0.20$

Approximation:

$$Kb \cong \frac{x^2}{0.20}$$

$x^2 = 0.20\ K_b$

$[OH^-] = \sqrt{0.20\ Kb}$

$[OH^-] = \sqrt{0.20\ (2.174 \times 10^{-11})}$

$[OH^-] = 2.085 \times 10^{-6}$ M

$[OH^-] = 2.1 \times 10^{-6}$ M *Both the 0.20 M and the Ka used in calculating Kb limit us to* *__2 SD's__*.

NOTE: In many problems, finding $[OH^-]$ is only the first step. Often you have to find the pH. Then you would use the process $[OH^-]$ → pOH → pH

Kb From pH and Concentration

Eg.) At a certain temp, a 0.20 M solution of K_2SO_3 has a pH of 10.25. Calculate the Kb of SO_3^{2-} at this temp.

1. Identify SO_3^{2-} as a weak base (When K_2SO_3 is dissociated, it yields K^+(a spectator) and SO_3^{2-})

2. $[OH^-]$ can be obtained from pH (pH → pOH → $[OH^-]$)

pH = 10.25 so pOH = 14.00 – 10.25 = 3.75
$[OH^-]$ = antilog (-pOH) = antilog (-3.75) = $\underline{1.778 \times 10^{-4}\ M}$

3. Write <u>hydrolysis</u> equation and an ICE table. (It is called *hydrolysis* this time because SO_3^{2-} is an <u>ion</u>.)
We know the *initial* [SO_3^{2-}] is 0.20M and the *equilibrium* [OH^-] is 1.778×10^{-4} M:

	SO_3^{2-}	+ H_2O ⇆	HSO_3^- +	OH^-
[I]	0.20		0	0
[C]				
[E]				1.778×10^{-4}

So, from this, the change in conc. [C] of OH^- is "+ 1.778×10^{-4}" and using the coefficient ratios we can insert the [C]'s for the other species and calculate the equilibrium concentrations [E]'s:

	SO_3^{2-}	+ H_2O ⇆	HSO_3 +	OH^-
[I]	0.20		0	0
[C]	$- 1.778 \times 10^{-4}$		$+ 1.778 \times 10^{-4}$	$+ 1.778 \times 10^{-4}$
[E]	**0.1998**		**1.778×10^{-4}**	**1.778×10^{-4}**

4. Now we write the Kb expression and substitute the values from the [E]'s in our ICE table:

$$K_b = \frac{[HSO_3^-]\,[OH^-]}{[SO_3^{2-}]} = \frac{(1.778 \times 10^{-4})^2}{(0.199822)} = 1.5825 \times 10^{-7}$$

We round it to 1.6×10^{-7} because the 0.20M and the pH given both had 2 SD's

So:

Kb of SO_3^{2-} at the temperature given is = 1.6×10^{-7}