

K_a & K_b for Weak acids and Bases

Reminder: pH of SA's

$[H_3O^+] = [\text{acid}]$ **strong** means 100% ionized

so, to find pH of 0.100 M HCl

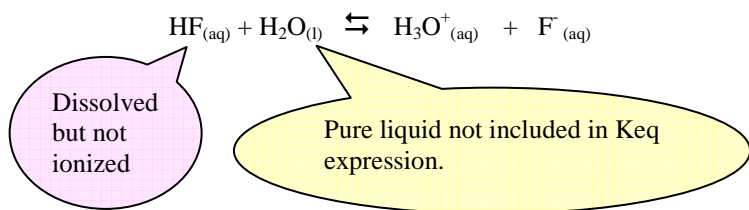
$[H_3O^+] = 0.100 \text{ M}$

pH = 1.000

For weak acids $[H_3O^+] \ll [\text{acid}]$

Eg.) What is pH of 0.10 M HF?

Look at equilibrium for **Weak Acid HF**



$K_{eq} = \frac{[H_3O^+][F^-]}{[HF]}$ for WA's Keq is called **K_a** (*acid* ionization constant)

- see acid table for list of K_a 's.

higher $K_a \rightarrow$ stronger acid

lower $K_a \rightarrow$ weaker acid

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

Essentially **zero**
molecular HCl

-Discuss Relative Strengths of Oxyacids

Calculations Using K_a (Used for Weak Acids)

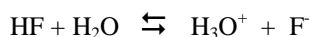
$[H_3O^+]$ from K_a (pH from K_a)

1. $[H_3O^+]$ from K_a and Original concentration (C_o)

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

WA

1. Write out equilibrium equation for *ionization*



2. Ice table

$$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$$

[I]	0.10		0	0
[C]	-x		+x	+x
[E]	0.10 - x		x	x

3. Ka expression: $K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$

$$K_a = \frac{(x)(x)}{0.10 - x}$$

4. Substitute

$$K_a = \frac{x^2}{0.10}$$

(Assume $0.10 - x \cong 0.10$)5. Solve for x ($[\text{H}_3\text{O}^+]$)

$$K_a = \frac{x^2}{0.100}$$

$$\text{So } x^2 = 0.10 K_a$$

$$[\text{H}_3\text{O}^+] = x = \sqrt{0.10 K_a}$$

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

$$[\text{H}_3\text{O}^+] = 5.9 \times 10^{-3} \text{ M}$$

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

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

You **must** state this assumption here!

Ka from Acid Table

Do ex. 74 & 75 Pg. 152After Questions 74 & 75Short cut for **multiple choice Only!!**

For WA $[\text{H}_3\text{O}^+] = \sqrt{C_o K_a}$

“root” a “coka”
(beer) (cola)

C_o is Original
Acid
Concentration

NOTE: In W.R. questions, full solution **must** be shown including the assumption!

Eg.) Find pH of 2.0 M acetic acid (*Multiple Choice Question*)

1. First $[\text{H}_3\text{O}^+] = \sqrt{C_o K_a}$

$$= \sqrt{2.0 (1.8 \times 10^{-5})}$$

$$[\text{H}_3\text{O}^+] = 6.0 \times 10^{-3} \text{ M}$$

Ka from
Acid Table

2. Find pH = $-\log (6.0 \times 10^{-3})$

$$\text{pH} = 2.22$$

2 SD's. The “2.0 M” was
2 SD's and the Ka was 2 SD's

Try using this for a
SA!!

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+} ($\text{Fe}(\text{H}_2\text{O})_6^{3+}$) could be found in $\text{Fe}(\text{H}_2\text{O})_6\text{Br}_3$ (also called FeBr_3)
 or $\text{Fe}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ (also called $\text{Fe}(\text{NO}_3)_3$)

Aluminum (hexaaquoaluminum) Al^{3+} ($\text{Al}(\text{H}_2\text{O})_6^{3+}$) could be found in $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$ (also called AlCl_3)

Do ex. 79 & 81, Pg. 152

More Ka Calculations:

Ka from pH

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

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 $[\text{H}_3\text{O}^+]$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \text{antilog} (-\text{pH}) \\ &= \text{antilog} (-1.620) \\ [\text{H}_3\text{O}^+] &= 2.399 \times 10^{-2} \text{ M} \end{aligned}$$

This is the
 $[\text{H}_3\text{O}^+]$ at
 equilibrium

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

	HA	+	H ₂ O	↔	H ₃ O ⁺	+	A ⁻
[I]	0.350				0		0
[C]							
[E]					2.399×10^{-2}		

Now, you can see that the change in concentration [C] of $[\text{H}_3\text{O}^+]$ is $+ 2.399 \times 10^{-2} \text{ M}$ and using the mole ratios (mole bridges) in the balanced equation, you can figure out the [C]'s for the A^- and the HA:

	$-2.399 \times 10^{-3}\text{M}$		$+ 2.399 \times 10^{-2}\text{M}$		$+ 2.399 \times 10^{-2}\text{M}$
	HA	+	H ₂ O	↔	H ₃ O ⁺ + A ⁻
[I]	0.350				0
[C]	$- 2.399 \times 10^{-2}$				$+ 2.399 \times 10^{-2}$
[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.

$$\begin{array}{ccccccc} & -2.399 \times 10^{-2} \text{M} & & + 2.399 \times 10^{-2} \text{M} & & + 2.399 \times 10^{-2} \text{M} & \\ & \text{HA} & + & \text{H}_2\text{O} & \rightleftharpoons & \text{H}_3\text{O}^+ & + & \text{A}^- \\ \text{[I]} & 0.350 & & & & 0 & & 0 \\ \text{[C]} & -2.399 \times 10^{-2} & & & & + 2.399 \times 10^{-2} & & + 2.399 \times 10^{-2} \\ \text{[E]} & 0.326 & & & & 2.399 \times 10^{-2} & & 2.399 \times 10^{-2} \end{array}$$

3. Write K_a expression & substitute values.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(2.399 \times 10^{-2})^2}{0.326} = 1.7653 \times 10^{-3} \text{ and expressing in 3SD's, the answer is:}$$

$$K_a = 1.77 \times 10^{-3}$$

For those that want a short-cut for multiple choice:

K_a from $[\text{H}_3\text{O}^+]$:

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{(\text{Co} - [\text{H}_3\text{O}^+])}$$

Don't forget this

OK for multiple choice ONLY!

Don't rearrange $[\text{H}_3\text{O}^+] = \sqrt{C_o K_a}$

Was derived using an assumption which may NOT be valid!

Do Ex. 77 & 80 on p. 152 SW

To Calculate C_o (conc. of acid needed) from pH & K_a

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

- First change pH to $[\text{H}_3\text{O}^+]$
 $[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH})$
 $= \text{antilog}(-2.69)$
 $[\text{H}_3\text{O}^+] = 2.0417 \times 10^{-3} \text{ M}$ (notice that the given pH limits us to 2SD's, but keep more in your calculations.)
- Write out ionization equilibrium with an ICE TABLE. You can insert 2.0417×10^{-3} for equilibrium $[\text{H}_3\text{O}^+]$. And since our **unknown** is the initial [HCOOH], we put in an " C_o " for the [I] of HCOOH:

$$\begin{array}{ccccccc} & \text{HCOOH} & + & \text{H}_2\text{O} & \rightleftharpoons & \text{H}_3\text{O}^+ & + & \text{HCOO}^- \\ \text{[I]} & C_o & & & & 0 & & 0 \\ \text{[C]} & & & & & & & \\ \text{[E]} & & & & & 2.0417 \times 10^{-3} & & \end{array}$$

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 ₂ O	↔	H ₃ O ⁺	+	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 ₂ O	↔	H ₃ O ⁺	+	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 K_a expression. Substitute equilibrium concentrations in. Find K_a for $HCOOH$ on the acid table:

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

Find K_a on Acid Table

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

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

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

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

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

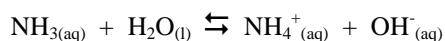
$$C_o = 2.52 \times 10^{-2} \text{ M}$$

$$C_o = 2.5 \times 10^{-2} \text{ M or } 0.025 \text{ M (remember, we are restricted to 2 SD's)}$$

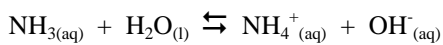
Do Ex. 76 & 78 on p. 152 of SW.

Now For Bases

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



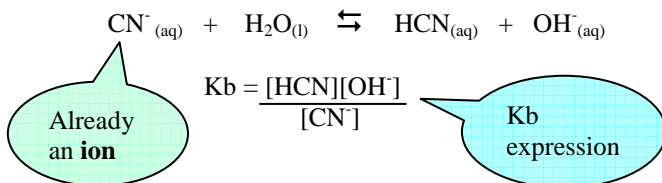
Equilibrium constant – called base ionization constant (K_b)



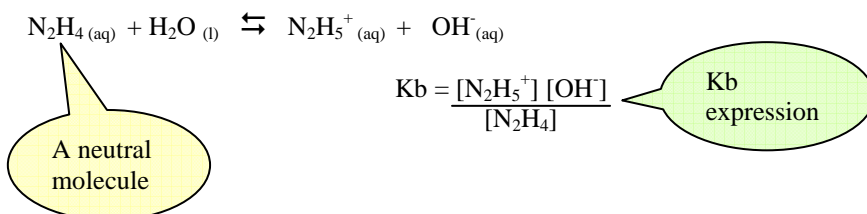
Kb expression:
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

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^-**



Ionization of N_2H_4 (weak base)



Do Ex 32 on p. 128 of SW.

How to Find Kb using Acid Table

(not shown directly)

Derivation

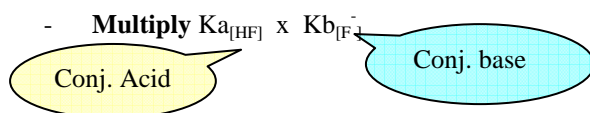
- Look at **hydrolysis** of **base F^-** : $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

$$K_b(\text{F}^-) = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$

- Look at **ionization** the weak **acid HF**: $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$

$$K_a(\text{HF}) = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

- **Multiply $K_{a[\text{HF}]}$ x $K_{b[\text{F}^-}]$**



$$K_{a[\text{HF}]} \times K_{b[\text{F}^-]} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \times \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] \text{ (notice that } [\text{HF}] \text{ and } [\text{F}^-] \text{ will cancel.)}$$

or
$$K_{a(\text{HF})} \times K_{b(\text{F}^-)} = K_w$$

$$K_{a(\text{HF})} \times K_{b(\text{F}^-)} = K_w$$

$$\text{Or } K_{b(\text{F}^-)} = \frac{K_w}{K_{a(\text{HF})}}$$

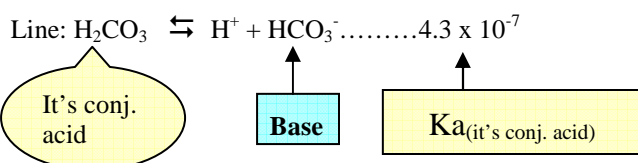
In general:

$$K_{b(\text{weak base})} = \frac{K_w}{K_{a(\text{it's conj. acid})}}$$

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 K_a of it's conjugate acid is on the **far right** of the same line.
4. Use equation: $K_{b(\text{base})} = \frac{K_w}{K_{a(\text{conj. acid})}}$

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



$$K_b(\text{HCO}_3^-) = \frac{K_w}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Find K_b of SO_3^{2-}

Similarly : If K_b (base) given

$$K_{a(\text{weak acid})} = \frac{K_w}{K_{b(\text{it's conj. Base})}}$$

Eg.) The K_b for base B^- is 2.73×10^{-9}

Find the K_a for the acid HB

3 sig. Digs.

$$K_{a(\text{HB})} = \frac{K_w}{K_{b(\text{B}^-)}} = \frac{1.00 \times 10^{-14}}{2.73 \times 10^{-9}} = 3.66 \times 10^{-6}$$

NOTES:

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

Calculations Involving K_b

Given: [Base] & K_b → Find $[\text{OH}^-]$ → or find pOH → or find pH

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

Dissociation of $\text{KNO}_2 \rightarrow \text{K}^+ + \text{NO}_2^-$

Neutral
spectator
(discard)

Weak base

1. Find K_b of NO_2^-

$$K_b(\text{NO}_2^-) = \frac{K_w}{K_a(\text{HNO}_2)}$$

$$= \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}}$$

$$K_b(\text{NO}_2^-) = 2.174 \times 10^{-11}$$

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

	NO_2^-	$+ \text{H}_2\text{O} \rightleftharpoons$	HNO_2	$+ \text{OH}^-$
[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^-	$+ \text{H}_2\text{O} \rightleftharpoons$	HNO_2	$+ \text{OH}^-$
[I]	0.20		0	0
[C]	-x		+x	+x
[E]	0.20 - x		x	x

3. K_b Expression:

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} \quad \text{at equilibrium}$$

On the next page, we substitute the [E]’s into the K_b expression (*Don’t forget, we are in “baseland” not “acidland” now!*)

Substitute: $K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$ or $K_b = \frac{x^2}{(0.20 - x)}$

Original
conc. of
 NO_2^- (Co)

Assume that
 $0.20 - x \approx 0.20$

Approximation:

$$K_b \approx \frac{x^2}{0.20}$$

$$x^2 = 0.20 K_b$$

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

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

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

$$[\text{OH}^-] = 2.1 \times 10^{-6} \text{ M} \quad \text{Both the } 0.20 \text{ M and the } K_a \text{ used in calculating } K_b \text{ limit us to } \underline{2 \text{ SD's.}}$$

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

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 K_b of SO_3^{2-} at this temp.

- Identify SO_3^{2-} as a weak base (When K_2SO_3 is dissociated, it yields K^+ (a spectator) and SO_3^{2-})
- $[\text{OH}^-]$ can be obtained from pH ($\text{pH} \rightarrow \text{pOH} \rightarrow [\text{OH}^-]$)

$$\text{pH} = 10.25 \text{ so } \text{pOH} = 14.00 - 10.25 = 3.75$$

$$[\text{OH}^-] = \text{antilog}(-\text{pOH}) = \text{antilog}(-3.75) = 1.778 \times 10^{-4} \text{ M}$$

- Write hydrolysis equation and an ICE table. (It is called *hydrolysis* this time because SO_3^{2-} is an ion.)
We know the *initial* $[\text{SO}_3^{2-}]$ is 0.20M and the *equilibrium* $[\text{OH}^-]$ is $1.778 \times 10^{-4} \text{ M}$:

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

$$K_b = \frac{[\text{HSO}_3^-][\text{OH}^-]}{[\text{SO}_3^{2-}]} = \frac{(1.778 \times 10^{-4})^2}{(0.199822)} = 1.5825 \times 10^{-7}$$

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 $= 1.6 \times 10^{-7}$

Short Cut for Multiple Choice:

$$K_b = \frac{[\text{OH}^-]^2}{(C_o - [\text{OH}^-])}$$

Like Weak acids:

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{(C_o - [\text{H}_3\text{O}^+])}$$

Rd. pg. 128 – 129 & 152-153

Do Ex. 84, 87, 88, & 89 on p. 153 of SW

- Do worksheet on Ka, Kb calculations