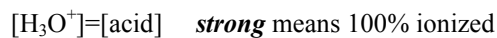


## Tutorial 4: $K_a$ & $K_b$ for Weak acids and Bases

Reminder: pH of SA's



so, to find pH of 0.100 M HCl

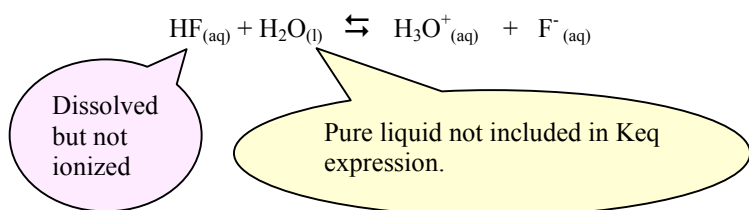
$$[\text{H}_3\text{O}^+] = 0.100 \text{ M}$$

$$\text{pH} = 1.000$$

For weak acids  $[\text{H}_3\text{O}^+] \ll [\text{acid}]$

Eg.) What is pH of 0.10 M HF?

Look at equilibrium for **Weak Acid HF**



$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

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)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]}$  = called "very large!"

Essentially zero molecular HCl

**-Discuss Relative Strengths of Oxyacids**

### Calculations Using $K_a$ (Used for Weak Acids)

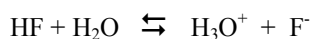
**$[\text{H}_3\text{O}^+]$  from  $K_a$  (pH from  $K_a$ )**

1.  $[\text{H}_3\text{O}^+]$  from  $K_a$  and Original concentration ( $C_0$ )

eg.) Find the  $[\text{H}_3\text{O}^+]$  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  $0.10 - x \approx 0.10$  )You **must** state this assumption here!5. Solve for x ( $[\text{H}_3\text{O}^+]$ )

$$K_a = \frac{x^2}{0.100} \quad \text{So } x^2 = 0.10 K_a$$

$$[\text{H}_3\text{O}^+] = x = \sqrt{0.10 K_a}$$
$$= \sqrt{0.10 (3.5 \times 10^{-4})}$$

Ka from Acid Table

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

~ 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!**NOTE:** Ions which act as acids can come from compounds.Eg.) See table ~ ammonium ion  $\text{NH}_4^+$ - can be found in  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , etc....ferric ( hexaaquoiron)  $\text{Fe}^{3+}$  ( $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ) could be found in  $\text{Fe}(\text{H}_2\text{O})_6\text{Br}_3$  (also called  $\text{FeBr}_3$ ) or  $\text{Fe}(\text{H}_2\text{O})_6(\text{NO}_3)_3$  (also called  $\text{Fe}(\text{NO}_3)_3$ )Aluminum (hexaaquoaluminum)  $\text{Al}^{3+}$  ( $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ) could be found in  $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$  (also called  $\text{AlCl}_3$ )**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  $[\text{H}_3\text{O}^+]$ 

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH})$$
$$= \text{antilog}(-1.620)$$

$$[\text{H}_3\text{O}^+] = 2.399 \times 10^{-2} \text{ M}$$

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

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

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

[I]	0.350		0	0
[C]				
[E]			$2.399 \times 10^{-2}$	

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

$$-2.399 \times 10^{-2}M \quad + 2.399 \times 10^{-2}M \quad + 2.399 \times 10^{-2}M$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

[I]	0.350		0	0
[C]	$- 2.399 \times 10^{-2}$		$+ 2.399 \times 10^{-2}$	$+ 2.399 \times 10^{-2}$
[E]			$2.399 \times 10^{-2}$	

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.

$$-2.399 \times 10^{-2}M \quad + 2.399 \times 10^{-2}M \quad + 2.399 \times 10^{-2}M$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

[I]	0.350		0	0
[C]	$- 2.399 \times 10^{-2}$		$+ 2.399 \times 10^{-2}$	$+ 2.399 \times 10^{-2}$
[E]	0.326		$2.399 \times 10^{-2}$	$2.399 \times 10^{-2}$

3. Write  $K_a$  expression & substitute values.

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

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

### To Calculate $C_o$ ( conc. of acid needed) form pH & $K_a$

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

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

$$[H_3O^+] = \text{antilog}(-\text{pH})$$

$$= \text{antilog}(-2.69)$$

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

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

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

[I]	$C_o$		0	0
[C]				
[E]			$2.0417 \times 10^{-3}$	

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

	HCOOH	+	H <sub>2</sub> O	↔	H <sub>3</sub> O <sup>+</sup>	+	HCOO <sup>-</sup>
[I]	C <sub>o</sub>				0		0
[C]	$- 2.0417 \times 10^{-3}$				$+ 2.0417 \times 10^{-3}$		$+ 2.0417 \times 10^{-3}$
[E]					$2.0417 \times 10^{-3}$		

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

	HCOOH	+	H <sub>2</sub> O	↔	H <sub>3</sub> O <sup>+</sup>	+	HCOO <sup>-</sup>
[I]	C <sub>o</sub>				0		0
[C]	$- 2.0417 \times 10^{-3}$				$+ 2.0417 \times 10^{-3}$		$+ 2.0417 \times 10^{-3}$
[E]	$C_o - 2.0417 \times 10^{-3}$				$2.0417 \times 10^{-3}$		$2.0417 \times 10^{-3}$

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):

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

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

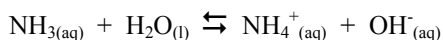
$$C_o = 2.3159 \times 10^{-2} + 2.0417 \times 10^{-3}$$

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

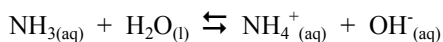
$$C_o = 2.5 \times 10^{-2} \text{ M or } 0.025 \text{ M (remember, we are restricted to 2 SD's)}$$

### Now For Bases

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

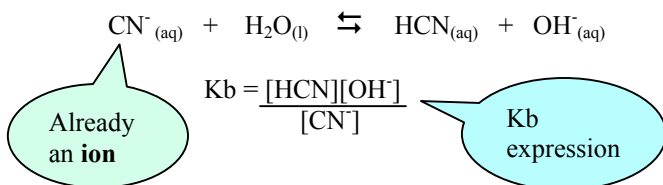
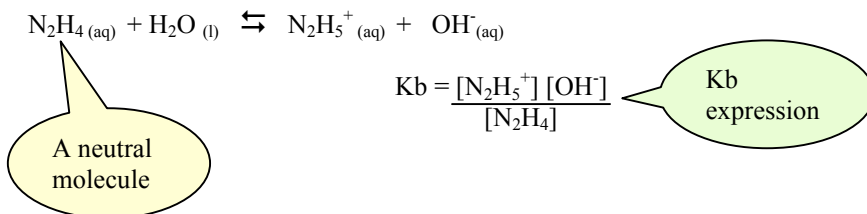


Equilibrium constant – called base ionization constant ( $K_b$ )



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

**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  $K_b$ .

Eg.) **Hydrolysis of  $\text{CN}^-$** **Ionization of  $\text{N}_2\text{H}_4$  (weak base)****How to Find  $K_b$  using Acid Table**

(not shown directly)

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

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

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

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

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

Conj. Acid

Conj. base

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

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

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

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

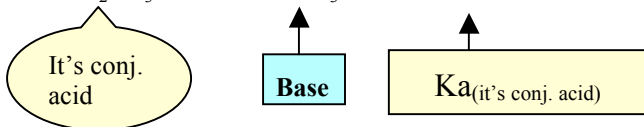
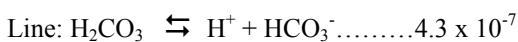
In general:

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

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  $\text{HCO}_3^-$ : ( find  $\text{HCO}_3^-$  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  $\text{SO}_3^{2-}$

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  $\text{B}^-$  is  $2.73 \times 10^{-9}$

Find the  $K_a$  for the acid  $\text{HB}$

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  $\text{OH}^-$  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  $\text{KNO}_2$  (*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

$$\begin{aligned} &1. \text{ Find } K_b \text{ of } \text{NO}_2^- \\ &K_b(\text{NO}_2^-) = \frac{K_w}{K_a(\text{HNO}_2)} \\ &= \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} \\ &K_b(\text{NO}_2^-) = 2.174 \times 10^{-11} \end{aligned}$$

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

$$\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$$

[I]	0.20		0	0
[C]				
[E]				

We can let “x” equal the moles/L of  $\text{NO}_2^-$  which hydrolyze as the reaction reaches equilibrium. Using the mole ratios in the equation and calculating [E]’s we get:

$$\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$$

[I]	0.20		0	0
[C]	-x		+x	+x
[E]	<b>0.20 - x</b>		<b>x</b>	<b>x</b>

3.  $K_b$  Expression:

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

We substitute the [E]’s into the  $K_b$  expression

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

Original  
conc. of  
 $\text{NO}_2^-$  ( $C_0$ )

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  $[\text{OH}^-] \rightarrow \text{pOH} \rightarrow \text{pH}$

### **$K_b$ From pH and Concentration**

Eg.) At a certain temp, a 0.20 M solution of  $\text{K}_2\text{SO}_3$  has a pH of 10.25. Calculate the  $K_b$  of  $\text{SO}_3^{2-}$  at this temp.

- Identify  $\text{SO}_3^{2-}$  as a weak base (When  $\text{K}_2\text{SO}_3$  is dissociated, it yields  $\text{K}^+$  (a spectator) and  $\text{SO}_3^{2-}$ )
- $[\text{OH}^-]$  can be obtained from pH ( $\text{pH} \rightarrow \text{pOH} \rightarrow [\text{OH}^-]$ )

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

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

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

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$$

[I]	0.20		0	0
[C]				
[E]				$1.778 \times 10^{-4}$

So, from this, the change in conc. [C] of  $\text{OH}^-$  is “+  $1.778 \times 10^{-4}$ ” and using the coefficient ratios we can insert the [C]’s for the other species and calculate the equilibrium concentrations [E]’s:

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$$

[I]	0.20		0	0
[C]	$-1.778 \times 10^{-4}$		$+1.778 \times 10^{-4}$	$+1.778 \times 10^{-4}$
[E]	<b>0.1998</b>		<b><math>1.778 \times 10^{-4}</math></b>	<b><math>1.778 \times 10^{-4}</math></b>

4. Now we write the  $K_b$  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  $1.6 \times 10^{-7}$  because the 0.20M and the pH given both had 2 SD’s

So:

$$K_b \text{ of } \text{SO}_3^{2-} \text{ at the temperature given is } = 1.6 \times 10^{-7}$$