$K_aK_b = K_w$

Proof:

$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$

Recall, at 25°C:

$Kw = [H_3O^+][OH^-]$

$[H_3O^+] = [OH^-] = 10^{-7}$ M

$Kw = (10^{-7})(10^{-7}) = 10^{-14}$

Consider the dissociation of any acid:

$HX + H_2O \rightleftarrows H_3O^+ + X^-$

$$Ka = \frac{[H_3O^+][X^-]}{[HX]}$$

Consider the reaction of a basic anion with water:

$X^- + H_2O \rightleftarrows HX + OH^-$

$$Kb = \frac{[HX][OH^-]}{[X^-]}$$

$$KaKb = \frac{[H_3O^+][X^-][HX][OH^-]}{[HX]\ [X^-]}$$

$KaKb = [H_3O^+][OH^-] = Kw$

at 25°C $KaKb = 10^{-14}$

USE KaKb = Kw to solve for Kb given only Ka

The acid and base in this equation will be conjugate acid-base pairs

example: The Ka for NH_4^+ is 5.6×10^{-10}. What is the Kb for NH_3 ?

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$$Kb(NH_3) = \frac{Kw}{Ka(NH_4^+)} = \frac{10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$

pH of solutions containing an ion
which can act as an acid and an ion which can act as a base

NH_4CH_3COO (s)

acidic or basic?

$NH_4CH_3COO (s) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$

- Consider $NH_4^+(aq)$:

$NH4^+(aq) + H2O (l) \rightleftarrows NH3 (aq) + H3O^+ (aq)$

$Ka (NH4^+) = 5.6 \times 10^{-10}$

- Consider $CH3COO^-(aq)$:

$CH3COO^-(aq) + H2O (l) \rightleftarrows CH3COOH (aq) + OH^- (aq)$

$$Kb (CH3COO^-) = \frac{Kw}{Ka (CH3COOH)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Since Ka = Kb the pH = 7.0 (neutral)

If Ka > Kb then the solution would be acidic **pH < 7**

If Ka < Kb then the solution would be basic **pH > 7**

$K_aK_b = K_w$ SAMPLE CALCULATIONS

1. Complete the following chart:

ACID	Ka	BASE	Kb
HBr			
HSO_4^-			
HNO_2			
H_2CO_3			
NH_4^+			
HS^-			

2. Consider a solution containing 1.0 M CN^- (aq). Find its pH.

CN^- (aq) + HOH (l) ⇄ HCN (aq) + OH^- (aq)

3. Consider a solution containing 1.0 M CH_3COO^-(aq). Find its pH and $[H_3O^+]$.

CH_3COO^-(aq) + HOH (l) ⇄ HCH_3COO(aq) + OH^- (aq)

4. Consider a 1.0 M solution with $[H_3O^+] = 2.4 \times 10^{-12}$. Calculate the Kb.

?? (aq) + HOH (l) ⇄ ?? (aq)+ OH^- (aq)

5. Consider a 0.25 M solution with $[H_3O^+] = 6.3 \times 10^{-11}$. Calculate the Kb.

?? (aq) + HOH (l) ⇄ ?? (aq) + OH^- (aq)

$K_aK_b = K_w$ SAMPLE CALCULATIONS

1. Complete the following chart:

Ka	ACID	BASE	Kb
~infinity	HBr	Br-	0
1.2×10^{-2}	HSO_4^-	SO_4^{-2}	8.3×10^{-13}
4.6×10^{-4}	HNO_2	NO_2^-	2.2×10^{-11}
4.3×10^{-7}	H_2CO_3	HCO_3^-	2.3×10^{-8}
5.6×10^{-10}	NH_4^+	NH_3	1.8×10^{-5}
1.3×10^{-13}	HS^-	S^{-2}	7.7×10^{-2}

NOTE THAT FROM THE TOP TO THE BOTTOM OF THE LIST

THE ACIDS GO FROM STRONGEST TO WEAK (best to least conductor)

THE BASES GO FROM WEAK TO STRONGEST (least to best conductor)

2. Consider a solution containing 1.0 M CN^- (aq). Find its pH.
IGNORE CATION!

	CN^- (aq)	+ HOH (l)	⇄	HCN (aq)	+	OH^- (aq)
I	1.0 M	X		--------		------
R	-y	X		+y		+y
E	1.0-y	X		y		y

$Kb = \frac{[HCN][OH^-]}{[CN^-]}$ $= Kw/Ka$ $= 10^{-14} / 4.9 \times 10^{-10}$

$= 2.0 \times 10^{-5}$

$= \frac{y^2}{1.0-y}$ Assume that y <<1.0

$y^2 = 2.0 \times 10^{-5}$

$y = 4.5 \times 10^{-3}$ so the assumption is valid (meaning that subtracting y would NOT have changed our answer in the denominator, above)

$[OH^-] = y = 4.5 \times 10^{-3}$ pOH = 2.35 (2 sig figs) pH = 11.65 (BASIC!)

3. Consider a solution containing 1.0 M $CH_3COO^-(aq)$. Find its pH and $[H_3O^+]$.

IGNORE CATION!

	$CH_3COO^-(aq)$	+ HOH (l)	⇄ CH_3COOH (aq)	+ OH^- (aq)
I	1.0 M	X	--------	------
R	-y	X	+y	+y
E	1.0-y	X	y	y

$Kb = \frac{[HCH_3COO][OH^-]}{[CH_3COO^-]} = Kw/Ka = 10^{-14} / 1.8 \times 10^{-5}$

$= 5.6 \times 10^{-10} = \frac{y^2}{1.0-y}$ Assume that y <<1.0

$y^2 = 5.6 \times 10^{-10}$

$y = 2.4 \times 10^{-5}$ assumption valid

$= [OH^-]$

pOH = 4.62 (2 sig figs)

pH = 9.38 (BASIC!)

4. Consider a 1.0 M solution with $[H_3O^+] = 2.4 \times 10^{-12}$. Calculate the Kb.

So pH = 11.62 (BASIC!)

pOH = 2.38

$[OH-] = 4.2 \times 10^{-3}$

I have represented this value as “y” in the table below

	?? (aq)	+ HOH (l)	⇄ ?? (aq)	+ OH^- (aq)
I	1.0 M	X	--------	------
R	-y	X	+y	+y
E	1.0-y	X	y	y

$Kb = \frac{(4.2 \times 10^{-3})^2}{1.0 - 4.2 \times 10^{-3}}$

$= 1.8 \times 10^{-5}$

If we wanted to figure out which base it was…

$Kb = \frac{Kw}{Ka}$ $1.8 \times 10^{-5} = \frac{1.0 \times 10^{-14}}{Ka}$

$Ka = 5.6 \times 10^{-10} = NH_4^+$

So the base was NH_3 !!!!!

5. Consider a 0.25 M solution with $[H_3O^+] = 6.3 \times 10^{-11}$. Calculate the Kb.

$[H_3O^+] = 10^{-10.20} = 6.3 \times 10^{-11}$
pH = 10.20 (BASIC!)
pOH = 3.80 (2 sig figs)
$[OH^-] = 1.6 \times 10^{-4}$

	?? (aq)	+ HOH (l) ⇄	?? (aq)	+ OH^- (aq)
I	0.25 M	X	--------	------
R	-y	X	+y	+y
E	0.25-y	X	y	y

Where Y represents $[OH^-] = 1.6 \times 10^{-4}$

$$Kb = \frac{y^2}{0.25-y}$$

$$= \frac{(1.6 \times 10^{-4})^2}{0.25 - 1.6 \times 10^{-4}}$$

$$= 1.0 \times 10^{-7}$$

Ka Kb = Kw

If $Kb = 1.0 \times 10^{-7}$

Then $Ka = 1.0 \times 10^{-7}$

The identity of the acid with $Ka = 1.0 \times 10^{-7}$ is HSO_3^-

So therefore the base with $Kb = 1.0 \times 10^{-7}$ is SO_3^{-2}

HYDROLYSIS

-a reaction between an ion and water which alters the $[OH^-]$ and $[H^+]$ in the resulting solution.

example:

CN^- (aq) + HOH (l) ⇄ HCN (aq) + OH^- (aq)

Note: CN^- (aq) hydrolysis produces a basic solution

Typical anion hydrolysis:

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

example:

NH_4^+ (aq) + HOH (l) ⇄ H_3O^+ (aq) + NH_3 (aq)

Note: NH_4^+ (aq) hydrolysis produces an acidic solution

Typical cation hydrolysis:

$$Kh = Ka = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

NOT ALL IONS HYDROLYZE!!!

example:

Cl^- (aq) + HOH (l) ⇄ HCl (aq) + OH^- (aq)

Kb = Kw / Ka
= 10^{-14} / infinity
= 0
K <<1 therefore reactants are preferred

This hydrolysis reaction does not proceed. HCl is a strong acid and will dissociate 100%.

Anions incapable of hydrolysis:

Cl^-, HSO_4^-, I^-, Br^-, NO_3^-. ClO_4^-

Cations incapable of hydrolysis:

Na^+, K^+, Li^+, Cs^+, Fr^+, Rb^+, Ca^{+2}, Ba^{+2}

HYDROLYSIS OF SALTS:

SALT	PARENT		pH of salt	HYDROLYSIS of ions
NaF	NaOH	strong base	basic pH >7	Na^+ - NO
	HF	weak acid		F^- - yes
KCl				
NH_4NO_3				
NH_4IO_3				
NH_4F				
NH_4CH_3COO				

SUMMARY: HYDROLYSIS OF SALTS:

1) Neither cation or anion hydrolyze: the salt solution will be neutral
2) Only the cation hydrolyzes: the solution will be acidic
3) Only the anion hydrolyzes: the solution will be basic
4) If both the cation and anion hydrolyze: ***the solution will be:***

acidic	if Ka > Kb
neutral	if Ka = Kb
basic	if Ka < Kb

Sample Calculation:

DETERMINE THE pH of a 0.06 M $NaCH_3COO$ SOLUTION.

HYDROLYSIS OF SALTS:

SALT	PARENT		pH of salt	HYDROLYSIS of ions
NaF	NaOH	strong base	basic pH >7	Na^+ - NO
	HF	weak acid		F^- - yes
KCl	HCl	strong acid	neutral pH = 7	K^+ - NO
	KOH	strong base		Cl^- - NO
NH_4NO_3	HNO_3	strong acid	acidic pH < 7	NH_4^+ - yes
	NH_4OH	weak base		NO_3^- - NO
NH_4IO_3	HIO_3	weak acid	**acidic**	NH_4^+ - yes
	NH_4OH	weak base		IO_3^- - yes

$NH_4^+ + HOH \rightleftarrows H_3O^+ + NH_3$

This Bronsted-Lowry equilibrium equation can also be written as:

$NH_4^+ + HOH \rightleftarrows H^+ + NH_4OH$

You should be OK with this second way to write the same reaction!

$Ka = 5.6 \times 10^{-10}$

$IO_3^- + HOH \rightleftarrows HIO_3 + OH^-$

$Kb = Kw / Ka = 5.9 \times 10^{-14}$

$Ka > Kb$

**Therefore Acidic!!!!!!!!! **

NH_4F	HF	weak acid	**acidic**	NH_4^+ - yes
	NH_4OH	weak base		F^- - yes

$NH_4^+ + HOH \rightleftarrows H_3O^+ + NH_3$

$Ka = 5.6 \times 10^{-10}$

$F^- + HOH \rightleftarrows HF + OH^-$

$Kb = Kw / Ka = 2.8 \times 10^{-11}$

$Ka > Kb$

**Therefore Acidic!!!!!!!!! **

SALT	PARENT		pH of salt	HYDROLYSIS of ions	
NH_4CH_3COO	HCH_3COO	weak acid	**neutral**	NH_4^+	- yes
	NH_4OH	weak base		CH_3COO^-	- yes

$NH_4^+ + HOH \rightleftarrows H_3O^+ + NH_3$

$Ka = 5.6 \times 10^{-10}$

$CH_3COO^- + HOH \rightleftarrows CH_3COOH + OH^-$

$Kb = Kw / Ka = 5.6 \times 10^{-10}$

Ka = Kb

**Therefore Neutral!!!!!!!!! **

SUMMARY: HYDROLYSIS OF SALTS:

1) Neither cation or anion hydrolyze: the salt solution will be neutral

2) Only the cation hydrolyzes: the solution will be acidic

3) Only the anion hydrolyzes: the solution will be basic

4) If both the cation and anion hydrolyze: the solution will be
   - acidic if $Ka > Kb$
   - neutral if $Ka = Kb$
   - basic if $Ka < Kb$

Sample Calculation:
DETERMINE THE pH OF A 0.06 M $NaCH_3COO$ SOLUTION.

HCH_3COO	weak acid	basic	Na^+	- NO
$NaOH$	strong base		CH_3COO^-	- yes

	CH_3COO^-	+ HOH ⇄	CH_3COOH	$+ OH^-$
I	0.06 M	XXX	---	---
R	-y	XXX	+y	+y
E	0.06 -y	XXX	y	y

$Kb = Kw / Ka = 5.6 \times 10^{-10}$

$5.6 \times 10^{-10} = y^2 / (0.06-y)$ assume $y << 0.06$

$3.4 \times 10^{-11} = y^2$

$y = 5.8 \times 10^{-6}$ M= $[OH^-]$

pOH = 5.24 pH = 8.76 Basic!!!

HYDROLYSIS REVIEW EXERCISE:

1 **Find the pH of:**

a) 0.50 M C_6H_5OH
b) 0.50 M KOH
c) 0.50 M H_2SO_4
d) 0.50 M HBr
e) 0.50 M H_2CO_3
f) 0.50 M NaCN
g) 0.50 M NH_4I
h) 0.50 M K_2SO_3

2 Give numerical proof to support your prediction of acidic, basic, or neutral character for the following compounds:

a) NH_4F
b) NH_4HS
c) $(NH_4)_3PO_4$

3 Will HPO_4^{-2} behave as an acid or a base in water at RTP? Show your proof.

HINTS for the HYDROLYSIS WORKSHEET:

THIS IS A DECEIVING WORKSHEET. YOU NEED TO KNOW A LOT TO COMPLETE THIS WORKSHEET. SUGGESTION FOR SUCCESS:
Make up flash cards of these questions and on the back of the flashcard write: whether it is a ***strong/weak acid/base,*** the ***dissocation equation*** and whether you will be ***calculating a Ka or a Kb***. Also keep track of how many significant figures you need to have throughout each question.

FRONT OF FLASHCARD:	BACK OF FLASHCARD:
a) Find the pH of 0.50 M C_6H_5OH	weak acid So use Ka to solve for [H+] C6H5OH ⇄ C6H5O- + H+
b) Find the pH of 0.50 M KOH	strong base therefore 100% dissoc. So no Ka or Kb needed [KOH] = [OH-]
c) Find the pH of 0.50 M H_2SO_4	strong DIPROTIC acid ***100% dissoc*** [H+] is not appreciably >K2 therefore a 2 stage dissoc ***IS necessary*** add $[H+]_1 + [H+]_2$ to find final [H+] and then pH
d) Find the pH of 0.50 M HBr	strong monoprotic acid therefore one step calc: 100% dissoc.
e) Find the pH of 0.50 M H_2CO_3	weak DIprotic acid [H+]> K2 therefore ignore second stage use Ka_1 to solve for [H+]
f) Find the pH of 0.50 M NaCN	parent base **NaOH:** strong base so: *Na+ will not hydrolyze* parent acid **HCN:** weak acid so: *SINGLE HYDROYSIS: CN^- only the ANION* solution will be basic; use Kb to solve $CN^- + HOH$ <==> $HCN + OH^-$
g) Find the pH of 0.50 M NH_4I	HI: strong acid parent (I- does not hydrolyze) NH_4OH or NH_3: weak base parent SINGLE HYDROYSIS: NH_4+ only the CATION solution will be acidic; use Ka to solve $NH_4^+ + HOH$ <==> $H^+ + NH_3$
h) Find the pH of 0.50 M K_2SO_3	KOH: strong base base (K+ does not hydrolyze) H2SO3: weak acid parent (you could also look at the HSO3- conj. and come to same conclusion) SINGLE HYDROYSIS: SO_3^{-2} only the ANION solution will be basic

Question 2:
DETERMINE SINGLE HYDROLYSIS (cation or anion) OR DOUBLE HYDROLYSIS (BOTH cation AND anion). Then use Ka versus Kb to determine acidic / basic character.
Question 3:
Use Ka of HPO_4^{-2} vs Kb of HPO_4^{-2} to determine if this amphiprotic ion is going to act as acid or base. ***Note that in question 2b*** you have to do something similar in addressing the fact that HS- could be an acid OR a base! And also consider the NH_4+ ion acting as an acid as well. Highest K value determines it.

HYDROLYSIS REVIEW EXERCISE KEY

1 **Find the pH of:**

a)	0.50 M C_6H_5OH	5.09 or 5.10	Acidic
b)	0.50 M KOH	13.70	Basic
c)	0.50 M H_2SO_4	0.29 (final [H+] = .512 M)	Acidic
d)	0.50 M HBr	0.30	Acidic
e)	0.50 M H_2CO_3	3.33	Acidic
f)	0.50 M NaCN	11.50 or 11.51	Basic
g)	0.50 M NH_4I	4.77 or 4.78	Acidic
h)	0.50 M K_2SO_3	10.35	Basic

2 Give numerical proof to support your prediction of acidic, basic, or neutral character for the following compounds:

a)	NH_4F	Acidic
b)	NH_4HS	Basic
c)	$(NH_4)_3PO_4$	Basic

3 Will HPO_4^{-2} behave as an acid or a base in water at RTP? Show your proof.

Base