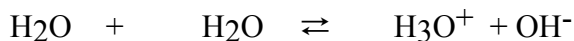


$$K_a K_b = K_w$$

Proof:



Recall, at 25°C:

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

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

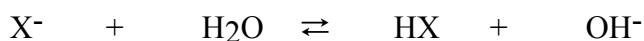
$$K_w = (10^{-7})(10^{-7}) = 10^{-14}$$

Consider the dissociation of any acid:



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

Consider the reaction of a basic anion with water:



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

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

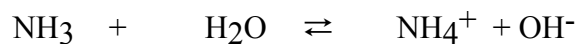
$$K_a K_b = [H_3O^+][OH^-] = K_w$$

$$\text{at } 25^\circ\text{C} \quad K_a K_b = 10^{-14}$$

USE $K_a K_b = K_w$ to solve for K_b given only K_a

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

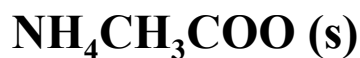
example: The K_a for NH_4^+ is 5.6×10^{-10} . What is the K_b for NH_3 ?



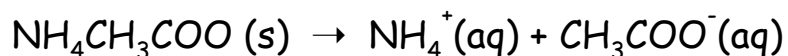
$$K_b(NH_3) = \frac{K_w}{K_a(NH_4^+)} = \frac{10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$

pH of solutions containing an ion

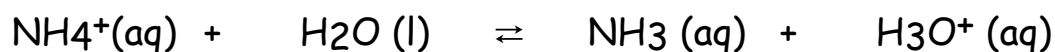
which can act as an acid and an ion which can act as a base



acidic or basic?

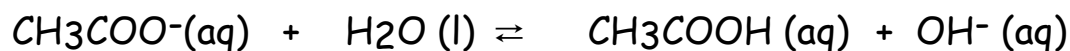


- Consider $\text{NH}_4^+(\text{aq})$:



$$K_a (\text{NH}_4^+) = 5.6 \times 10^{-10}$$

- Consider $\text{CH}_3\text{COO}^-(\text{aq})$:



$$K_b (\text{CH}_3\text{COO}^-) = \frac{K_w}{K_a (\text{CH}_3\text{COOH})} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Since $K_a = K_b$ the pH = 7.0 (neutral)

If $K_a > K_b$ then the solution would be acidic **pH < 7**

If $K_a < K_b$ then the solution would be basic **pH > 7**

$$K_a K_b = K_w$$

SAMPLE CALCULATIONS

1. Complete the following chart:

ACID	K_a	BASE	K_b
------	-------	------	-------

HBr

HSO_4^-

HNO_2

H_2CO_3

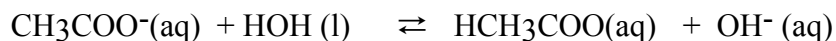
NH_4^+

HS^-

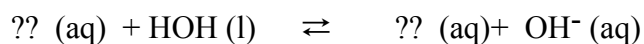
2. Consider a solution containing 1.0 M CN^- (aq). Find its pH.



3. Consider a solution containing 1.0 M CH_3COO^- (aq). Find its pH and $[\text{H}_3\text{O}^+]$.



4. Consider a 1.0 M solution with $[\text{H}_3\text{O}^+] = 2.4 \times 10^{-12}$. Calculate the K_b .



5. Consider a 0.25 M solution with $[\text{H}_3\text{O}^+] = 6.3 \times 10^{-11}$. Calculate the K_b .



$$K_a K_b = K_w$$

SAMPLE CALCULATIONS

1. Complete the following chart:

K_a	ACID	BASE	K_b
\sim 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 ₂ CO 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)	\rightleftharpoons	HCN (aq)	+	OH ⁻ (aq)
I	1.0 M	X		-----		-----
R	-y	X		+y		+y
E	1.0-y	X		y		y

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = K_w/K_a = 10^{-14} / 4.9 \times 10^{-10}$$

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

$$= \frac{y^2}{1.0-y}$$

$$\text{Assume that } y \ll 1.0$$

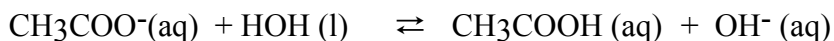
$$y^2 = 2.0 \times 10^{-5}$$

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

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

3. Consider a solution containing 1.0 M CH₃COO⁻(aq). Find its pH and [H₃O⁺].

IGNORE CATION!



I	1.0 M	X	-----	-----
R	-y	X	+y	+y
E	1.0-y	X	y	y

$$K_b = \frac{[\text{HCH}_3\text{COO}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = K_w/K_a = 10^{-14} / 1.8 \times 10^{-5}$$

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

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

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

assumption valid

$$= [\text{OH}^-]$$

$$\text{pOH} = 4.62 \text{ (2 sig figs)}$$

$$\text{pH} = 9.38 \text{ (BASIC!)}$$

4. Consider a 1.0 M solution with [H₃O⁺] = 2.4 x 10⁻¹². Calculate the K_b.

So pH = 11.62 (BASIC!)

$$\text{pOH} = 2.38$$

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

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

$$K_b = \frac{(4.2 \times 10^{-3})^2}{1.0 - 4.2 \times 10^{-3}} = 1.8 \times 10^{-5}$$

If we wanted to figure out which base it was...

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

$$K_a = 5.6 \times 10^{-10} = \text{NH}_4^+$$

So the base was NH₃ !!!!!

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

$$[H_3O^+] = 10^{-10.20} = 6.3 \times 10^{-11}$$

$$pH = 10.20 \text{ (BASIC!)}$$

$$pOH = 3.80 \text{ (2 sig figs)}$$

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



I	0.25 M	X	-----	-----
R	-y	X	+y	+y
E	0.25-y	X	y	y

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

$$\begin{aligned}
 K_b &= \frac{y^2}{0.25-y} \\
 &= \frac{(1.6 \times 10^{-4})^2}{0.25 - 1.6 \times 10^{-4}} \\
 &= 1.0 \times 10^{-7}
 \end{aligned}$$

$$K_a K_b = K_w$$

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

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

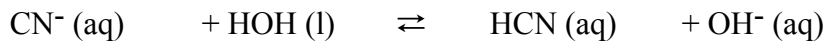
The identity of the acid with $K_a = 1.0 \times 10^{-7}$ is HSO_3^-

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

HYDROLYSIS

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

example:

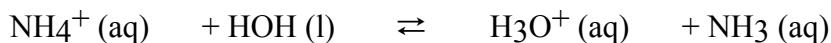


Note: CN^- (aq) hydrolysis produces a basic solution

Typical anion hydrolysis:

$$K_h = K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

example:



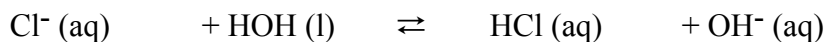
Note: NH_4^+ (aq) hydrolysis produces an acidic solution

Typical cation hydrolysis:

$$K_h = K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

NOT ALL IONS HYDROLYZE!!!

example:



$$\begin{aligned} K_b &= K_w / K_a \\ &= 10^{-14} / \text{infinity} \\ &= 0 \end{aligned}$$

$K \ll 1$ 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:

<u>SALT</u>	<u>PARENT</u>		<u>pH of salt</u>	<u>HYDROLYSIS of ions</u>
NaF	NaOH	strong base	basic pH > 7	Na ⁺ - NO
	HF	weak acid		F ⁻ - yes

KCl

NH₄NO₃

NH₄IO₃

NH₄F

NH₄CH₃COO

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 $K_a > K_b$
 - neutral** if $K_a = K_b$
 - basic** if $K_a < K_b$

Sample Calculation:

DETERMINE THE pH of a 0.06 M NaCH₃COO 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 ₄ NO ₃	HNO ₃	strong acid	acidic pH < 7	NH ₄ ⁺ - yes
	NH ₄ OH	weak base		NO ₃ ⁻ - NO
NH ₄ IO ₃	HIO ₃	weak acid	**acidic**	NH ₄ ⁺ - yes
	NH ₄ OH	weak base		IO ₃ ⁻ - yes



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



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

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

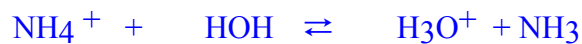


$$K_b = K_w / K_a = 5.9 \times 10^{-14}$$

$$K_a > K_b$$

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

NH ₄ F	HF	weak acid	**acidic**	NH ₄ ⁺ - yes
	NH ₄ OH	weak base		F ⁻ - yes



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



$$K_b = K_w / K_a = 2.8 \times 10^{-11}$$

$$K_a > K_b$$

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

SALT	PARENT		pH of salt	HYDROLYSIS of ions	
NH ₄ CH ₃ COO	HCH ₃ COO	weak acid	**neutral**	NH ₄ ⁺	- yes
	NH ₄ OH	weak base		CH ₃ COO ⁻	- yes
$\text{NH}_4^+ + \text{HOH} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$ $K_a = 5.6 \times 10^{-10}$					
$\text{CH}_3\text{COO}^- + \text{HOH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$ $K_b = K_w / K_a = 5.6 \times 10^{-10}$					
$K_a = K_b$ <p>**Therefore Neutral!!!!!!!!!! **</p>					

SUMMARY: HYDROLYSIS OF SALTS:

- Neither cation or anion hydrolyze: the salt solution will be **neutral**
- Only the cation hydrolyzes: the solution will be **acidic**
- Only the anion hydrolyzes: the solution will be **basic**
- If both the cation and anion hydrolyze:

the solution will be	
acidic	if $K_a > K_b$
neutral	if $K_a = K_b$
basic	if $K_a < K_b$

Sample Calculation:

DETERMINE THE pH OF A 0.06 M NaCH₃COO SOLUTION.

	HCH ₃ COO	weak acid		basic	Na ⁺	- NO
	NaOH	strong base			CH ₃ COO ⁻	- yes
	$\text{CH}_3\text{COO}^- + \text{HOH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$					
I	0.06 M	XXX		---	---	
R	-y	XXX		+y	+y	
E	0.06 -y	XXX		y	y	
$K_b = K_w / K_a = 5.6 \times 10^{-10}$ $5.6 \times 10^{-10} = y^2 / (0.06 - y) \quad \text{assume } y \ll 0.06$ $3.4 \times 10^{-11} = y^2$ $y = 5.8 \times 10^{-6} \text{ M} = [\text{OH}^-]$						
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 **dissociation 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:

- Find the pH of 0.50 M C₆H₅OH
- Find the pH of 0.50 M KOH
- Find the pH of 0.50 M H₂SO₄
- Find the pH of 0.50 M HBr
- Find the pH of 0.50 M H₂CO₃
- Find the pH of 0.50 M NaCN
- Find the pH of 0.50 M NH₄I
- Find the pH of 0.50 M K₂SO₃

BACK OF FLASHCARD:

weak acid So use Ka to solve for [H⁺]
C₆H₅OH ⇌ C₆H₅O⁻ + H⁺

strong base
therefore 100% dissociation. So no Ka or Kb needed
[KOH] = [OH⁻]

strong DIPROTIC acid 100% dissociation
[H⁺] is not appreciably > K₂
therefore a 2 stage dissociation **IS necessary**
add [H⁺]₁ + [H⁺]₂ to find final [H⁺] and then pH

strong monoprotic acid
therefore one step calculation: 100% dissociation.

weak Diprotic acid
[H⁺] > K₂ therefore ignore second stage
use Ka₁ to solve for [H⁺]

parent base **NaOH**: strong base so:
Na⁺ will not hydrolyze

parent acid **HCN**: weak acid so:
SINGLE HYDROLYSIS: CN⁻ only the ANION
solution will be basic; use Kb to solve
CN⁻ + HOH ⇌ HCN + OH⁻

HI: strong acid parent (I⁻ does not hydrolyze)
NH₄OH or NH₃: weak base parent
SINGLE HYDROLYSIS: NH₄⁺ only the CATION
solution will be acidic; use Ka to solve
NH₄⁺ + HOH ⇌ H⁺ + NH₃

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 HYDROLYSIS: SO₃²⁻ 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 HPO₄⁻² vs Kb of HPO₄⁻² 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 NH₄⁺ 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