

Chapter 17: Equilibria in Aqueous Solution: Part I

We have just finished discussing equilibrium in general (Ch. 17)

- Let us now apply what we learned about systems in equilibrium
- to a particular system : AQUEOUS SYSTEMS.

In aqueous systems^{in Ch. 17}: all the substances are dissolved in H₂O. (except H₂O)
However some substances are more ionic than others, and therefore will ionize (dissociate ≡ break into ions) better than others.

Consider HCl(aq) ⇌ H⁺(aq) + Cl⁻(aq) K_c: very large

$$K = K_c = \frac{[H^+][Cl^-]}{[HCl]} \text{ very large}$$

∴ at equilibrium we have much more H⁺, Cl⁻ ions than the undissociated HCl.

we know this to be true anyway because HCl is a strong one of the seven strong acids and dissociates nearly completely in aqueous solution. ∴ in solution we have lots of ions to conduct electricity well.

Consider CH₃COOH(aq) ⇌ H⁺(aq) + CH₃COO⁻(aq)
acetic acid acetate ion

$$K = K_c = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Note: we can calculate ΔG° for forward rxn at 25°C

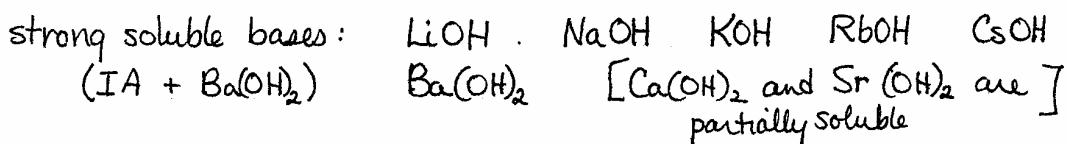
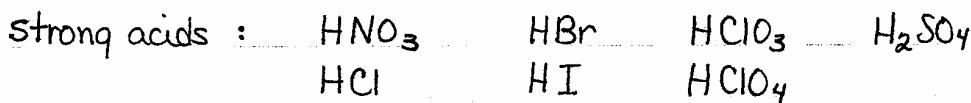
$$\begin{aligned}\Delta G^\circ &= -RT\ln K_{\text{forward}} \\ &= -(8.314 \times 10^{-3}) \\ &\quad \times 298 \times \ln 1.8 \times 10^{-5}\end{aligned}$$

= +27.1 kJ
∴ rxn is nonspont. as written

at equilibrium, we have much more undissociated CH₃COOH(aq) than H⁺ or CH₃COO⁻ ions - the CH₃COOH(aq) is dissolved in H₂O - but it is for the most part unionized.
∴ acetic acid is a weak electrolyte - a weak acid that does not conduct electricity very well in aqueous solution because there are not many ions to carry the current.

Review:

Strong electrolytes: compounds that ionize completely or nearly so.



soluble salts : IA and ammonium salts
 nitrates acetates chlorates perchlorates
 (chart on exam envelope lists insoluble salts
 and bases)

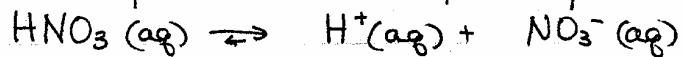
Weak electrolytes: compounds that conduct electricity poorly.

	weak bases (Appendix I)	weak acids (Appendix H)
know	✓ NH ₃ ammonia	✓ CH ₃ COOH acetic acid
	✓ (CH ₃)NH ₂ methyl amine	✓ H ₂ CO ₃ carbonic acid
	✓ (CH ₃) ₂ N dimethyl amine	✓ HF(aq) hydrofluoric acid
	✓ (CH ₃) ₃ N trimethyl amine	✓ HCN(aq) hydrocyanic acid
	N ₂ H ₄ hydrazine	✓ H ₂ S(aq) hydrosulfuric acid
		✓ lots more

Note: You are still responsible for nomenclature

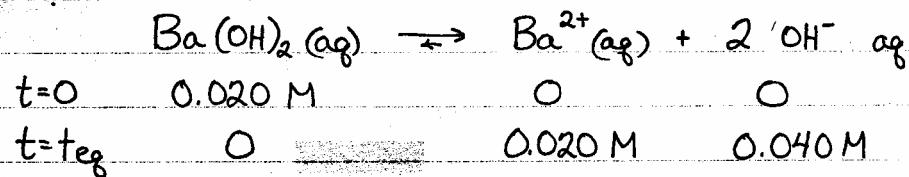
Calculation of ion concentrations for strong electrolytes:

Example: Consider 0.0100 M nitric acid: $\text{HNO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
 Nitric acid is a strong acid and breaks up entirely into its ions.

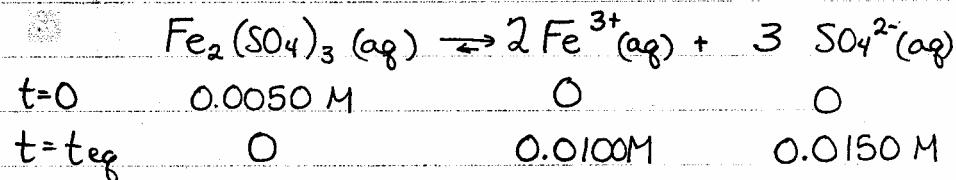


$\therefore [\text{H}^+] = 0.0100 \text{ M}$	$t=0$	0.0100	0	0
$[\text{NO}_3^-] = 0.0100 \text{ M}$	$t=\text{eq}$	0	0.0100 M	0.0100 M

Example: Consider 0.020 M $\text{Ba}(\text{OH})_2$: a strong soluble base

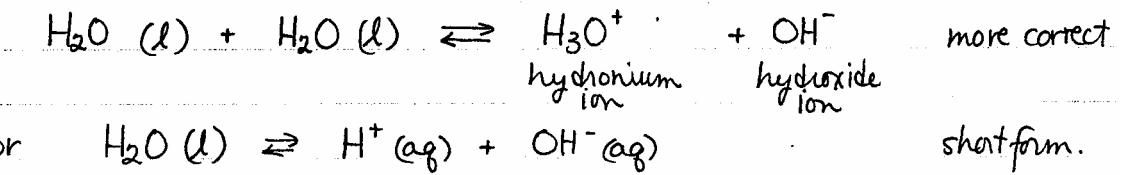


Example: Consider 0.0050 M $\text{Fe}_2(\text{SO}_4)_3$: a soluble salt



Ionization of Water

Pure water ionizes to some extent :



$$K_w = K_c = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

this is valid for
all dilute solutions
at 25°C .

\therefore in a neutral solution: $[\text{H}^+] = [\text{OH}^-] = x$

$$\therefore x^2 = 1.00 \times 10^{-14}$$

$$x = 1.00 \times 10^{-7} \text{ M} = [\text{H}^+] = [\text{OH}^-]$$

\therefore in any solution, if we know $[\text{H}^+]$, we can calculate $[\text{OH}^-]$.

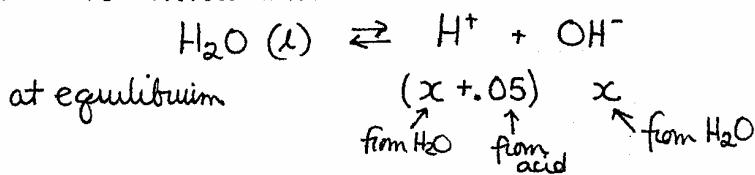
Example: Calculate the concentrations of H^+ and OH^- in 0.050 M HCl(aq).
we know HCl is a strong acid and dissociates "completely".

	HCl (aq)	\rightarrow	H^+ (aq)	$+ Cl^-$ (aq)
$t=0$	0.050		~0	0
$t=t_{eq}$	0		0.050	0.050

$\therefore [H^+] = 0.050 \text{ M}$ (we can ignore the contribution to $[H^+]$ by the dissociation of H_2O . see note)

$$\begin{aligned}\therefore [OH^-] &= \frac{K_w}{[H^+]} \\ &= \frac{1.00 \times 10^{-14} (\text{M}^2)}{[0.050 \text{ M}]} \\ &= 2.0 \times 10^{-13} \text{ M}\end{aligned}$$

step: Why can we ignore the contribution to $[H^+]$ by the ionization of H_2O ?
What is the contribution?



$$\begin{aligned}K_w &= 1.00 \times 10^{-14} = [H^+][OH^-] \\ \text{at } 25^\circ C &= (x + 0.05)(x) \\ 0 &= x^2 + 0.05x - 1.00 \times 10^{-14}\end{aligned}$$

$$\begin{aligned}x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-0.05 \pm \sqrt{(0.05)^2 + 4(1)(1 \times 10^{-14})}}{2} \\ &= \frac{-0.05 \pm 0.05}{2} \quad \text{this term is negligible} \\ &= 0, -0.05 \\ &\text{nonsense.}\end{aligned}$$

In fact, we know x cannot be 0 but must be some very small number $x \ll 0.05$. So we simplify the equation by saying $(x + 0.05) \cong 0.05$ since x is so small, and solve.

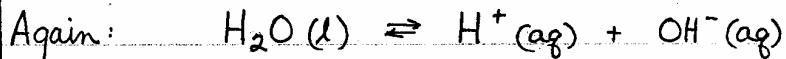
$$K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$$

$$= (x + 0.05)x$$

↑
ignore since is so small.

$2.0 \times 10^{-13} M = x = [OH^-] = [H^+]$ that was contributed by
the dissociation of water.

You will find we do these simplifications often for calculations involving weak acids and weak bases (recall water is a weak acid and a weak base).



Recall Le Chatelier's Principle: if H^+ or OH^- is added to the system the equilibrium will shift to make more $H_2O(l)$.

∴ in acidic solution: we add H^+ , the equilibrium shifts and $[OH^-] \downarrow$

$$\therefore [H^+] > [OH^-]$$

∴ in basic solution: we add OH^- , and $[H^+] \downarrow$

$$[OH^-] > [H^+]$$

pH Scale

Concentrations of ions (aq) can vary over many orders of magnitude.

A convenient way of expressing this is by using logarithms.

$$pX = -\log_{10} X$$

$$\therefore pH = -\log_{10} [H^+]$$

$$pOH = -\log_{10} [OH^-]$$

$$pAg = -\log_{10} [Ag^+]$$

generally

Consider the pH scale: it ranges from 0 → 14. [Recall $10^{-14} = [H^+][OH^-]$]

	basic	neutral	acidic	
$[H^+]$	$10^{-14} M$	10^{-7}	10^{-2}	$10^0 = 1$
pH	14	7	2	0
$[OH^-]$	1 M	10^{-7}	10^{-12}	10^{-14}
pOH	0	7	12	14

Note: pH can be negative or > 14 for very acidic or basic samples.

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∴ Using either $K_w = 10^{-14} = [H^+][OH^-]$ and $14 = pH + pOH$
plus the definitions we can do the following examples:

① Calculate the pH of a solution in which $[H_3O^+] = 0.030\text{ M}$

$$pH = -\log(0.030) = -\log(3.0 \times 10^{-2}) = 1.52$$

② Calculate pOH of a solution where $[H_3O^+] = 1.0 \times 10^{-11}\text{ M}$

Two ways:

$$(i) [OH^-] = \frac{K_w}{1.0 \times 10^{-11}} = 1.0 \times 10^{-3}\text{ M} \quad \therefore pOH = -\log[OH^-] = 3$$

$$(ii) pH = -\log(1.0 \times 10^{-11}\text{ M}) = 11$$

$$\therefore pOH = 14 - pH = 3$$

③ The pH of a solution is 4.597. What is $[H_3O^+]$?

$$pH = 4.597$$

$$-\log_{10}[H^+] = 4.597$$

$$\log_{10}[H^+] = -4.597$$

$$[H^+] = 2.53 \times 10^{-5}\text{ M}$$

④ Calculate $[H_3O^+]$, pH, $[OH^-]$ and pOH for 0.020M $Ba(OH)_2$.

We recognize $Ba(OH)_2$ to be a strong ^{solute} base which dissociates nearly completely.

$$\therefore [OH^-] = 0.020\text{ M} \times 2 = 0.040\text{ M}$$

$$pOH = -\log[0.040] = 1.40$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.040} = 2.5 \times 10^{-13}$$

$$pH = -\log[H^+] \text{ or } 14 - pOH \\ = 12.60$$

More on pH :

pH of solutions is determined by

(1) indicators which turn color in specific pH ranges

(2) a pH meter which uses a glass electrode to sense H_3O^+ ions

It is calibrated using solutions of known pH.

It measures $-\log[H^+]$ directly.

1. Arrhenius Theory of Acid-Base Behavior

Examples

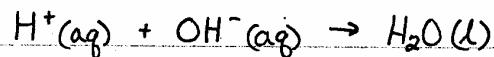


acid: species that contains H and produces H^+ in aqueous solution

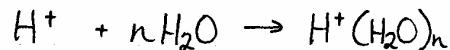


base: species that contains OH and produces OH^- in aqueous solution

acid-base reaction: reaction where H^+ and OH^- combine to form H_2O .
(neutralization)



Note: it is realized now that $\text{H}^+(\text{aq})$ does not exist as such. It is hydrated in water:



We represent this in equations by using the hydronium ion, H_3O^+ .
(In all of our balancing equations, though, it is easier to use H^+ .)

2. Bronsted-Lowry Theory

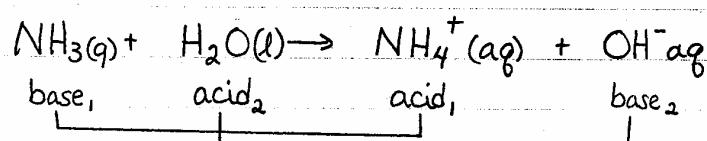
acid: a substance that donates a proton, H^+ i.e. a proton donor

∴ any substance containing hydrogen is a B.-L. acid.

base: a substance that accepts a proton i.e. a proton acceptor.

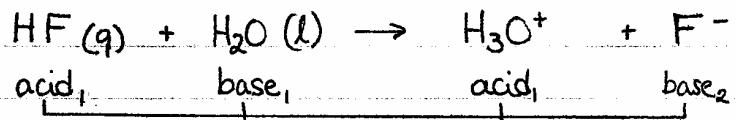
acid-base reaction: reaction in which a proton is transferred from an acid to a base.

Bronsted-Lowry theory is more general than Arrhenius theory! NH_3 is considered a base even though it has no OH group, because it accepts H^+ .



ACID
BASE
Reaction

Bronsted-Lowry acid-base reactions can be described in terms of CONJUGATE ACID-BASE PAIRS. These are species on opposite sides of the equation that differ by a proton. (H^+).

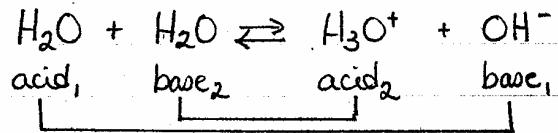


$\therefore \text{HF}$, F^- and H_3O^+ , H_2O are conjugate acid base pairs.
since they differ only by H^+ .

$\therefore \text{NH}_3$, NH_4^+ and H_2O , OH^- are also conjugate acid base pairs

Note: water can act as a base and as an acid in aqueous solutions.
It is called AMPHOTERIC. When the transfer involves a proton,
the term is amphiprotic.

IONIZATION OF WATER
(example of autoionization)



Examples of conjugate acid-base pairs:

ACID	CONJUGATE BASE
HCl	Cl^-
CH_3COOH	CH_3COO^-
H_2SO_4	HSO_4^-
HClO_4	ClO_4^-
H_2O	OH^-
H_3O^+	H_2O
NH_3	NH_2^- (not exist in water)
NH_4^+	NH_3
HSO_4^-	SO_4^{2-}

See also Table 17.2

How strong are these acids and their conjugate bases?

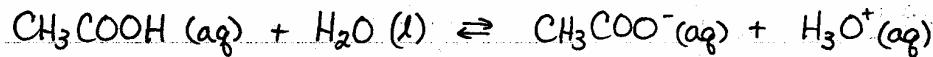
The stronger the acid, the more it wants to donate a proton.

The stronger the base, the more it wants to accept a proton.

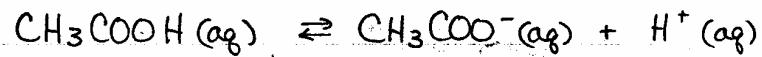
Generalization: The weaker an acid is, the greater is the base strength of its conjugate base. The weaker a base is, the greater is the acid strength of its conjugate acid.

Ionization Constants for Weak Monoprotic Acids and Weak Bases

There are many weak acids. As we saw earlier, dilute acetic acid (vinegar) dissociates only slightly in water to give ions



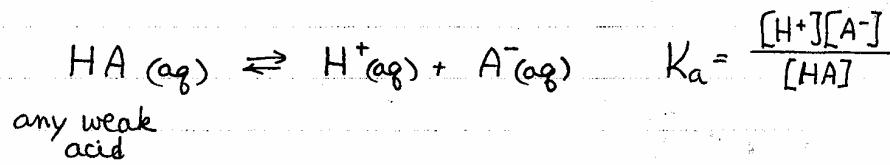
OR



$$K = K_c = K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \text{ ionization constant}$$

concentration acid

K_a , ionization constant, is the equilibrium constant for a specific equilibrium : The dissociation of a dissolved weak acid into its ions.



Note: Ionization constants, like other equilibrium constants, must be determined experimentally and are dependent on temperature.

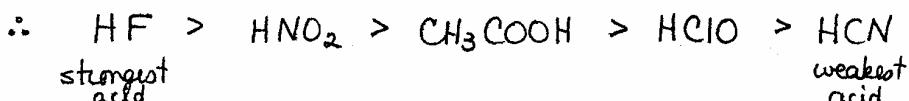
Consider the following :

K_a ↓ smaller weaker acid	HF	hydrofluoric acid	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4}$
	HNO_2	nitrous acid	$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$
	CH_3COOH	acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$
	HClO	hypochlorous acid	$\text{HClO} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]} = 3.5 \times 10^{-8}$
	HCN	hydrocyanic acid	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 4.0 \times 10^{-10}$

Which is the strongest acid? (Which is the acid when dissolved in water will dissociate the most to give the highest concentrations of ions and conduct the most electricity?) .

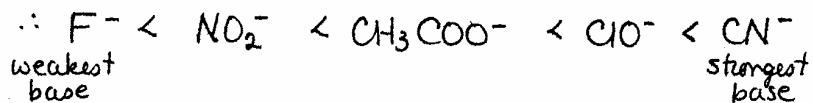
ANS. HF since K_a of HF is relatively the largest number.

It is still a small number \therefore at equilibrium, most of the acid exists as $\text{HF}(\text{aq})$ = it is dissolved but unionized. It is a weak acid.

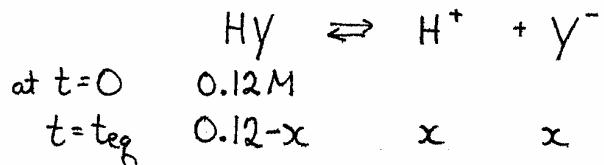


as K_a decreases, the acids become weaker.

Recall from Brønsted-Lowry theory, that the conjugate bases get stronger as acids get weaker (as $K_a \downarrow$)



Example: In a 0.12 M solution, a weak monoprotic (one H) acid, HY is 5.0% ionized. Calculate the ionization constant.



but what is x ? $5.0\% \text{ of } Hy = 0.050 \times 0.12M = 0.0060 M$

$$\therefore K_a = \frac{[H^+][Y^-]}{[HY]} = \frac{(0.0060)^2}{(0.12 - 0.006)} = 3.16 \times 10^{-4}$$

$$\therefore \text{at equilibrium: } [\text{H}^+] = [\text{Y}^-] = 0.0060$$

$$\therefore \text{pH of solution} = -\log [\text{H}^+] = 2.22$$

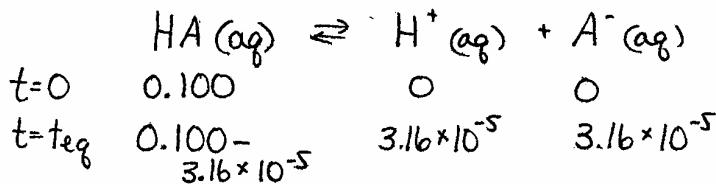
$$[\text{HY}] = 0.12 - x = 0.114 \text{ M}$$

It is also possible to calculate K_a given the pH of the solution and the initial concentration.

Example: What is the K_a for an unknown weak acid, HA, if the pH of a 0.100 M solution is 4.50?

$$\text{pH} = 4.50 \quad \therefore -\log [\text{H}^+] = 4.50 \\ [\text{H}^+] = 3.16 \times 10^{-5} \text{ M}$$

K_a is the equilibrium constant for the reaction:

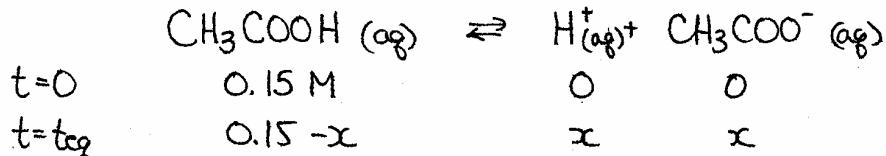


$$K_a = \frac{(3.16 \times 10^{-5})^2}{(0.100 - 3.16 \times 10^{-5})}$$

↑
neglect since is
a very small number compared to 0.100 M

$$= 9.99 \times 10^{-9}$$

Example: Calculate the concentrations of all species in 0.15 M acetic acid.
[you need to look up K_a for acetic acid = 1.8×10^{-5}]



$$\therefore K_a = 1.8 \times 10^{-5} = \frac{x^2}{(0.15 - x)} \\ = x^2 + 1.8 \times 10^{-5}x - 2.7 \times 10^{-6}$$

solving, $x = [\text{H}^+] = [\text{CH}_3\text{COO}^-] = 1.6 \times 10^{-3} \text{ M}$

$$[\text{CH}_3\text{COOH}] = 0.15 - x = 0.15$$



Therefore, the acid is so weak that it ionizes very little under these conditions. At equilibrium, the concentration of the undissociated acid is essentially the same as it was initially.

Rule of Thumb: If the K_a for the acid is $\sim 10^{-5}$ or less ~~or~~ AND if x is added to or subtracted from a comparatively large number, then x can be disregarded in the following term: $(x + \text{large number}) = (\text{large number})$.

Note: I suggest using the Rule of Thumb first if K_a is $\sim 10^{-5}$ or smaller and then solving for x . If x is much smaller than the initial concentration of acid (or base), the Rule of Thumb was OK to use.

To redo the problem:

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{(0.15-x)} \quad \text{but } K_a \sim 10^{-5} \therefore \text{use rule of thumb}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.15}$$

$$x = 1.6 \times 10^{-3} \text{ M} = [\text{H}^+] = [\text{CH}_3\text{COO}^-]$$

If we compare x with 0.15 we see that yes, $x \ll 0.15$ and the Rule of Thumb assumption is OK.

Now, providing the Rule of Thumb works - we can rearrange the formula above and solve for $[\text{H}^+] = x$

for a weak acid: $[\text{H}^+] = \sqrt{K_a [\text{acid}]_{\text{initial}}}$	if Rule of Thumb applies
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Example (continued) What is the percent ionization of 0.15 M CH_3COOH ?

$$\% \text{ionization} = \frac{[\text{acid}]_{\text{ionized}}}{[\text{acid}]_{\text{total}}} \times 100 = \frac{1.6 \times 10^{-3}}{0.15} \times 100 = 1.07 \%$$

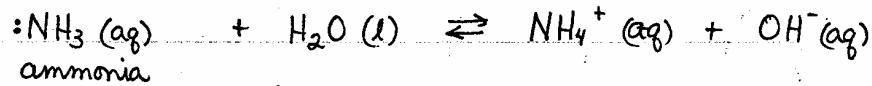
or
initial

Example (continued) What is the pH of a solution of 0.15 M CH_3COOH

$$\text{pH} = -\log [\text{H}^+] = -\log (1.6 \times 10^{-3}) = 2.80$$

We have emphasized the ionization of weak acids - what about weak bases?

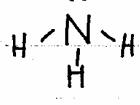
Consider :



$$K = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \quad (\text{by serendipity - the same value as } K_a \text{ for acetic acid})$$

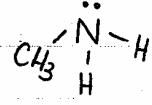
[refers to the equilibrium constant for ionization of a weak base]

Amines are weak bases that are derivatives of ammonia. They undergo the same kind of ionization reaction as ammonia.



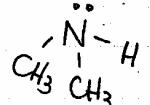
ammonia

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



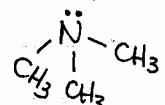
methyl amine

$$5.0 \times 10^{-4}$$



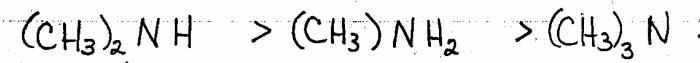
dimethylamine

$$7.4 \times 10^{-4}$$

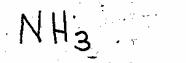


dimethylamine

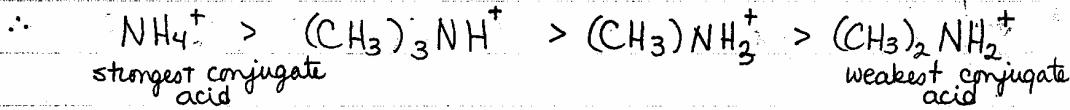
$$7.4 \times 10^{-5}$$



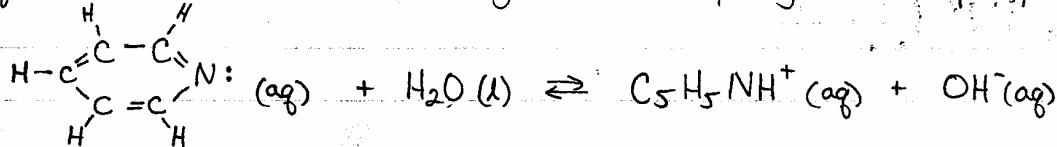
strongest base



weakest base



Example: Calculate the concentrations of various species in 0.15 M aqueous pyridine. Calculate the % ionization (extent of ionization) and pH of solution.



$t=0$ 0.15 M 0 0

$$t = t_{\text{eq}} \quad 0.15 - x \quad x \quad x$$

$$@ \quad K_b = 1.5 \times 10^{-9} = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

$$= \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

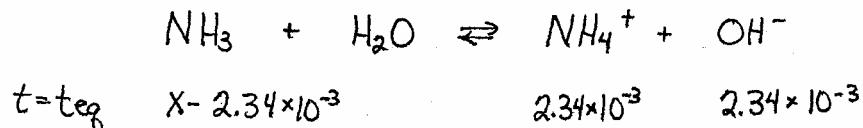
$$[\text{OH}^-] = [\text{C}_5\text{H}_5\text{NH}^+] \approx x = 1.5 \times 10^{-5} \text{ M}$$

$$[C_5H_5N] = 0.15 \text{ M}$$

(b) extent of ionization
 $\% \text{ ionization} = \frac{[\text{C}_5\text{H}_5\text{N}]_{\text{ionized}}}{[\text{C}_5\text{H}_5\text{N}]_{\text{total}}} \times 100 = \frac{1.5 \times 10^{-5}}{0.15} \times 100 = 0.01\%$

(c) $\text{pH} = 14 - \text{pOH}$
 $= 14 - (-\log(1.5 \times 10^{-5}))$
 $= 9.18$

Example: The pH of an aqueous ammonia solution is 11.37. Calculate the molarity of the solution. $K_b \text{ ammonia} = 1.8 \times 10^{-5}$



$$\text{pH} = 11.37$$

$$\therefore \text{pOH} = 14 - 11.37 = 2.63$$

$$[\text{OH}^-] = 2.34 \times 10^{-3} \text{ M}$$

$$\therefore K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$= \frac{(2.34 \times 10^{-3})^2}{X - 2.34 \times 10^{-3}}$$

omit

$$X = 0.30 \text{ M}$$

since $K_b \approx 10^{-5}$

From these examples, we can rearrange the equation

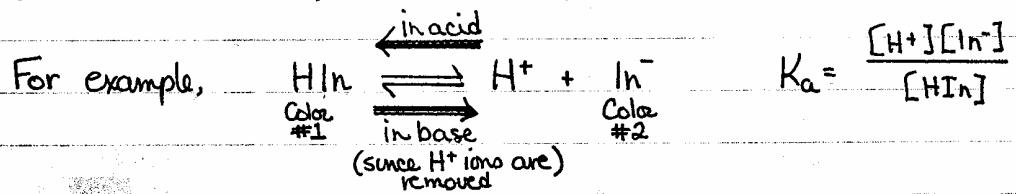
$$K_b = \frac{[\text{OH}^-]^2}{[\text{base}]} \quad \text{if Rule of Thumb holds}$$

for a weak base: $[\text{OH}^-] = \sqrt{K_b [\text{base}]_{\text{initial}}}$ using Rule of Thumb.

Acid-Base Indicators

- indicators are organic dyes ; color depends on the concentration of H_3O^+ ions, or pH in the solution
 - used in acid-base titrations to determine endpoints

Many indicators are weak acids. Different indicators change colors in different pH ranges depending on their K_a .



Solving the K_a expression for the ratio, $\frac{[In^-]}{[HIn]} = \frac{K_a}{[H^+]}$

Rule of Thumb: $\frac{[In^-]}{[HIn]} \leq \frac{1}{10}$ Color #1 predominates

$$\frac{[\text{In}^-]}{[\text{HIn}]} \geq 10 \quad \text{Color #2 predominates}$$

$\frac{[\text{In}^-]}{[\text{HIn}]} \approx 1$ or $[\text{H}^+] \approx K_a$, this is the endpoint

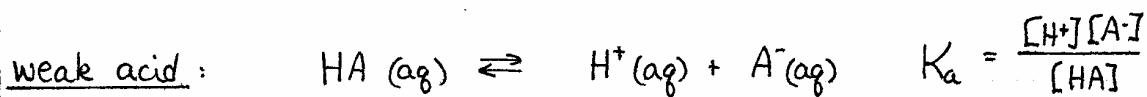
Examples:	Indicator	Color in more acidic range (due to HIn)	pH range	Color in more basic range (due to In ⁻)
		Color #1		Color #2
	methyl violet	yellow	0-2	purple
	methyl orange	pink	3.1-4.4	yellow
	litmus	red	4.7-8.2	blue
	phenolphthalein	colorless	8.3-10.0	red

Example: $K_a = 7.9 \times 10^{-8}$ for bromothymol blue - an indicator expressed as HIn .

HIn molecules are yellow, In⁻ ions are blue. What is color of indicator when [H⁺] is 10⁻⁴

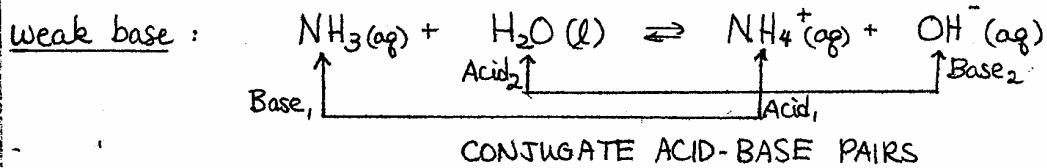
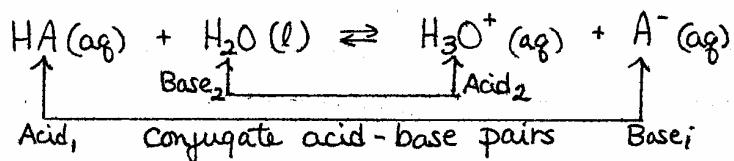
$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}^+]} = \frac{7.9 \times 10^{-8}}{1.0 \times 10^{-4}} = 7.9 \times 10^{-4} \quad \therefore [\text{HIn}] \text{ dominates; soln is yellow.}$$

Let's review what we have learned about the ionization of weak electrolytes:



OR

as the text book expresses it : HA reacts with H_2O thusly



Recall: conjugate acid-base pairs (Bronsted-Lowry Theory) differ only by a proton (H^+)

acid: wants to donate a proton. The stronger the acid, the more it wants to donate a proton. Strong acids donate their proton ie ionize almost completely.

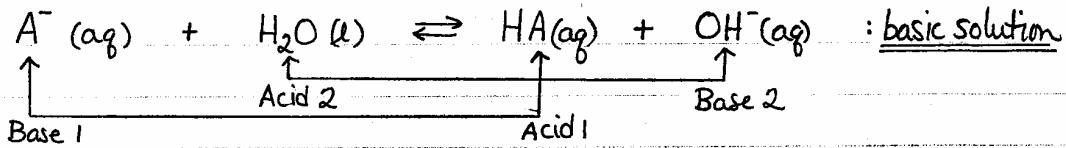
base: wants to accept a proton. The stronger the base, the more it wishes to accept a proton.

strong acids have weak conjugate bases.
strong bases have weak conjugate acids.

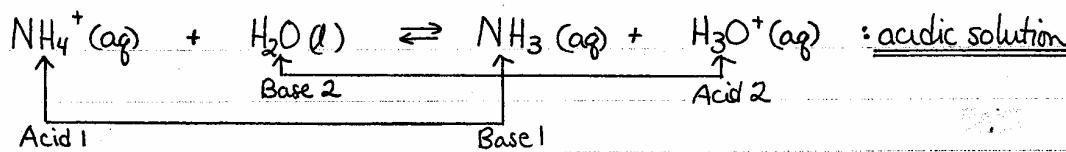
Therefore, the ionization of weak acids and weak bases can be thought of as acid-base reactions with amphoteric water playing the part of either an acid or a base.

Let's go a step further.

Consider A^- , the stronger conjugate base of the weak acid, HA. It can also participate in a kind of acid-base reaction with water.



Consider NH_4^+ , the stronger conjugate acid of the weak base, NH_3 .



These reactions of ions (from salts) are called hydrolysis reactions since one of the reactants is water. The stronger the ^{conjugate} acid or base, the more it will react with water to upset the OH^- / H^+ balance in water.

What are the equilibrium constants for the hydrolysis reactions?

ANS. we derive them from equilibrium constants we already know.

For an ion that is a stronger base (derived from a weak acid, HA)

$$K_b(A^-) = \frac{[HA][OH^-]}{[A^-]} \quad A^- \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons HA \text{ (aq)} + OH^- \text{ (aq)}$$

$$\text{but we know } K_a = \frac{[H^+][A^-]}{[HA]} \quad HA \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons H_3O^+ \text{ (aq)} + A^- \text{ (aq)}$$

$$\text{and } K_w = [H^+][OH^-] \quad H_2O \text{ (l)} + H_2O \text{ (l)} \rightleftharpoons H_3O^+ \text{ (aq)} + OH^- \text{ (aq)}$$

$$\therefore K_b(A^-) = \frac{K_w}{K_a \text{ for HA}} \times \frac{[H^+][OH^-]}{[H^+][A^-]} \quad \therefore$$

Likewise, for an ion that is a stronger acid (NH_4^+) derived from weak base (NH_3)

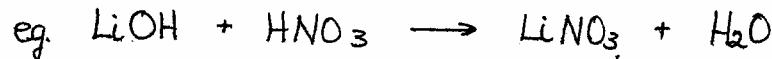
$$K_a(NH_4^+) = \frac{K_w}{K_b} \quad (\text{prove this to yourself})$$

What does this mean? If we dissolve a soluble salt - a source of cations and anions - in water, these ions may react with water to make acidic, neutral, or basic solutions. It depends on the acid strength or base strength of the ions.

I Salts of Strong Acids and Strong Soluble Bases

Recall: strong acids: HNO_3 , H_2SO_4 , HClO_4 , HClO_3 , HCl , HBr , HI

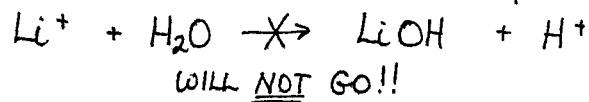
strong soluble bases: LiOH , NaOH , KOH , RbOH , CsOH , $\text{Ba}(\text{OH})_2$
 $[\text{Ca}(\text{OH})_2 \text{ and } \text{Sr}(\text{OH})_2]$



salts: formed when any strong acid reacts with any strong, soluble base
 eg LiNO_3 , $\text{Ba}(\text{ClO}_4)_2$, RbCl , CaBr_2 etc

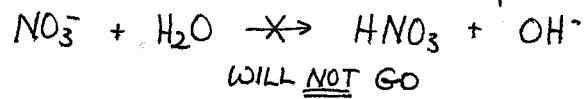
Consider $\text{LiNO}_3 \text{ (aq)} \rightleftharpoons \text{Li}^+ \text{ (aq)} + \text{NO}_3^- \text{ (aq)}$
 a soluble salt - dissociates [~]totally.

Li^+ (from LiOH) is a weak acid derived from strong base



cannot react with water to form undissociated
 LiOH - too weak

NO_3^- (from HNO_3) is a weak base derived from a strong acid



Cannot react with water to form undissociated
 HNO_3 - too weak.

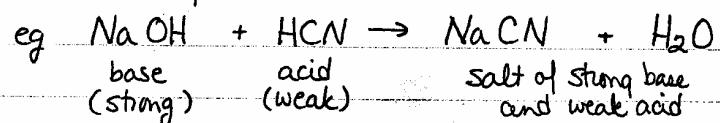
∴ the solution of $\text{LiNO}_3 \text{ (aq)}$ is neutral - neither cation nor anion will react with water to upset H^+/OH^- balance of water.

III Salts of Strong Bases and Weak acids

Examples : NaCN, KCH₃COO, Ba(ClO)₂, RbF

cations : derived from strong base

anion : derived from weak acid

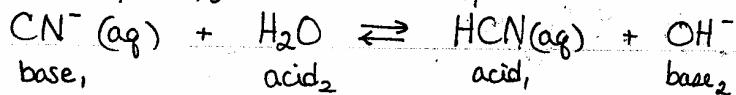


The salt is soluble and dissociates ~completely.



Na^+ is a very weak acid and does not react with water

but CN^- ^{is a weak base} hydrolyzes in water to produce a basic solution



the hydrolysis equilibrium constant $K_b = \frac{K_w}{K_a \text{ for HCN}}$

for the base, CN^-

$$= \frac{1.00 \times 10^{-14}}{4.0 \times 10^{-10}}$$

$$= 2.5 \times 10^{-5}$$

In general, $K_b \text{ for anion} = \frac{K_w}{K_a \text{ for weak acid}}$

Example : Calculate the hydrolysis constant for the anion, F^-

$$K_b \text{ for } \text{F}^- = \frac{K_w}{K_a \text{ for HF}} = \frac{1.00 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

Let's compare solutions of NaCN and NaF

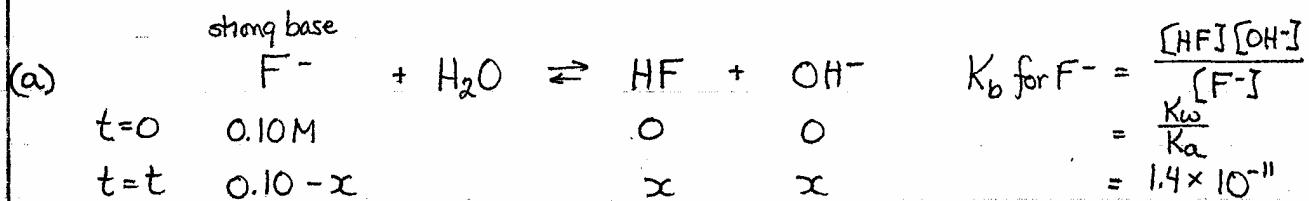
We just calculated that K_b for $\text{F}^- \ll K_b$ for CN^-

$\therefore \text{CN}^-$ hydrolyzes much more (reacts with H_2O much more) than F^- does to form OH^- ions

\therefore a solution of NaCN is more basic than NaF and

Now let's do the calculations. $\therefore \text{CN}^-$ is a much stronger base than F^-

Example: Calculate $[\text{OH}^-]$, pH and % hydrolysis for the fluoride ion in 0.10 M NaF solution and CN^- ion in 0.10M NaCN.



$$K_b = 1.4 \times 10^{-11} = \frac{x^2}{0.10-x} \quad \text{Rule of Thumb}$$

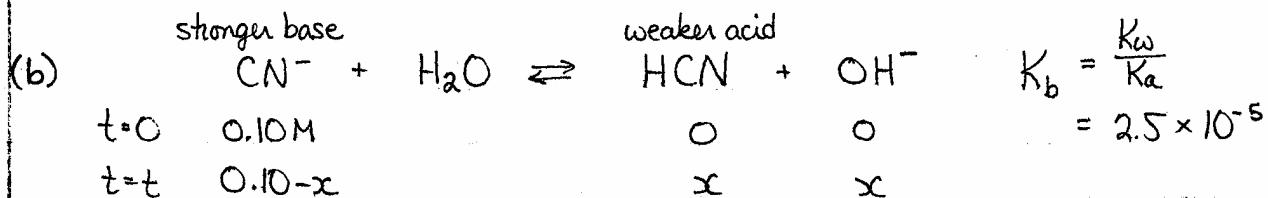
$$x^2 = 1.4 \times 10^{-12}$$

$$[\text{OH}^-] = x = 1.2 \times 10^{-6} \text{ M} \quad \text{or } [\text{OH}^-] = \sqrt{\frac{K_w}{K_a}} [\text{salt}]$$

$$\text{pOH} = 5.92$$

$$\text{pH} = 8.08$$

$$\% \text{ hydrolysis} = \frac{[\text{F}^-]_{\text{hydrolyzed}}}{[\text{F}^-]_{\text{total}}} \times 100 = \frac{1.2 \times 10^{-6}}{0.1} \times 100 = 1.2 \times 10^{-3} \%$$



$$K_b = 2.5 \times 10^{-5} = \frac{x^2}{0.10-x} \quad \text{Rule of Thumb}$$

$$x^2 = 2.5 \times 10^{-6}$$

$$[\text{OH}^-] = x = 1.6 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.80$$

$$\text{pH} = 11.20$$

$$\% \text{ hydrolysis} = \frac{[\text{CN}^-]_{\text{hydrolyzed}}}{[\text{CN}^-]_{\text{total}}} \times 100 = \frac{1.6 \times 10^{-3}}{0.10} \times 100 = 1.6 \%$$

Let's compare the two salts by making a chart:

Solution	K_a parent acid	K_b	$[OH^-] (M)$	pH	% hydrolysis
0.10 M NaF	7.2×10^{-4} (HF)	1.4×10^{-11} (F ⁻)	1.2×10^{-6}	8.08	1.2×10^{-3}
0.10 M NaCN	4.0×10^{-10} (HCN)	2.5×10^{-5} (CN ⁻)	1.6×10^{-3}	11.20	1.6

We see from K_a that HCN is much weaker acid than HF
 $\therefore \text{CN}^-$ is much stronger base than F^-
 $\therefore \text{CN}^-$ hydrolyzes much more than F^-

III Salts of Weak Bases and Strong Acids

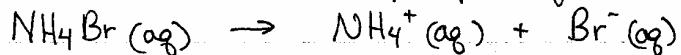
Examples : NH_4Cl , $(\text{CH}_3)_3\text{N}\text{HBr}$, NH_4NO_3

cations : derived from weak base

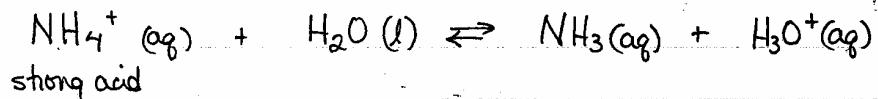
anion : derived from strong acid



The salt is soluble and dissociates \sim completely in aqueous solution.



Br^- is a very weak base and does NOT react with H_2O .
 but NH_4^+ is a ^{weak} strong acid ; it reacts with H_2O to form NH_3 and
 H_3O^+ ions.



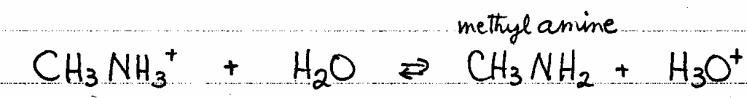
$$K_a \text{ for } \text{NH}_4^+ = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b \text{ for } \text{NH}_3}$$

$$= \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.56 \times 10^{-10}$$

In general, K_a for cation = $\frac{K_w}{K_b}$ for weak base

Example : Calculate the K_a for CH_3NH_3^+ ion



$$K_a = \frac{K_w}{K_b \text{ for } \text{CH}_3\text{NH}_2} = \frac{1.00 \times 10^{-14}}{5.0 \times 10^{-4}} = 2.0 \times 10^{-11}$$

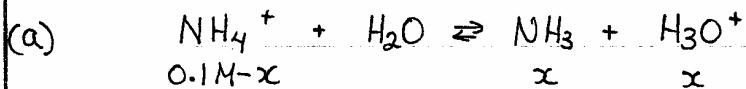
Example : Given 2 solutions that are 0.1 M in ammonium ion and 0.1 M in CH_3NH_3^+ ion respectively - which solution has the lower pH (which is more acidic) ?

The more acidic solution has the higher $[\text{H}^+]$ ∵ the cation that hydrolyzes to the greater extent produces more H^+ ions
 ∵ the larger K_a for the cation, the more it hydrolyzes and produces H^+ .
 ∵ the smaller K_b is for the base, the larger K_a is for cation and lower is pH of solution.

$$\begin{array}{ll} K_b & \\ \text{CH}_3\text{NH}_2 & 5.0 \times 10^{-4} \\ \text{NH}_3 & 1.8 \times 10^{-5} \end{array} \leftarrow \text{a solution of } \text{NH}_4^+ \text{ produces a lower pH.}$$

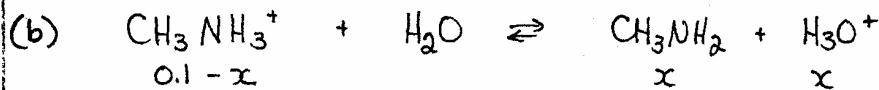
Example : Calculate the $[\text{H}^+]$, pH and percent hydrolysis for

- (a) ammonium ion in 0.1 M NH_4Br
 (b) CH_3NH_3^+ ion in 0.1 M $\text{CH}_3\text{NH}_3\text{Br}$
- $\left. \begin{matrix} & \\ & \end{matrix} \right\}$ both are soluble salts.



$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{K_a \text{ [acid]}} \quad \therefore \text{pH} = 5.13 \\ &= \sqrt{\frac{K_w}{K_b} [\text{NH}_4^+]} \\ &= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} (0.1)}} = 7.5 \times 10^{-6} \text{ M} \end{aligned}$$

$$\begin{aligned}\% \text{ hydrolysis of } \text{NH}_4^+ &= \frac{[\text{NH}_4^+] \text{ hydrolyzed}}{[\text{NH}_4^+] \text{ initial}} \times 100 \\ &= \frac{7.5 \times 10^{-6} \text{ M}}{0.10 \text{ M}} \times 100 \\ &= 7.5 \times 10^{-3} \%\end{aligned}$$



$$\begin{aligned}[\text{H}_3\text{O}^+] &= \sqrt{K_a [\text{acid}]} \quad \text{since Rule of Thumb will probably apply} \\ &= \sqrt{\frac{K_w}{K_b} [\text{NH}_4^+]} \\ &= \sqrt{\frac{1 \times 10^{-14}}{5 \times 10^{-9}} (0.1)}\end{aligned}$$

$$[\text{H}_3\text{O}^+] = 1.41 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.85$$

$$\begin{aligned}\% \text{ hydrolysis of } \text{CH}_3\text{NH}_2^+ &= \frac{[\text{CH}_3\text{NH}_2^+] \text{ hyd.}}{[\text{CH}_3\text{NH}_2^+] \text{ initial}} \times 100 \\ &= \frac{1.41 \times 10^{-6}}{0.1} \times 100 \\ &= 1.41 \times 10^{-3} \%\end{aligned}$$

\therefore a solution of NH_4^+ does indeed form a solution with a lower pH than does a solution of CH_3NH_3^+ since NH_4^+ hydrolyzes to a greater extent.

IV: Salts of Weak Bases and Weak Acids: (not for testing)

Examples: NH_4F , $\text{CH}_3\text{NH}_3\text{CN}$, $\text{NH}_4\text{CH}_3\text{COO}$

cation: derived from weak base

anion: derived from weak acid

What sets the pH of a solution of these salts since both the cation and the anion react with water re hydrolyze?

The ion that hydrolyzes to the greater extent controls the pH of solution.

① cation and anion hydrolyze to the same extent

$$K_a \text{ for cation} = K_b \text{ for anion}$$

$$\therefore K_b \text{ for base} = K_a \text{ for acid}$$

the solution is neutral :

example : $\text{NH}_4^+ \text{CH}_3\text{COO}^-$

$$K_a \text{ for } \text{NH}_4^+ = \frac{K_w}{K_b \text{ for } \text{NH}_3} = \frac{K_w}{1.8 \times 10^{-5}}$$

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

② cation hydrolyzes to a greater extent than anion

$$\therefore K_a \text{ for cation} > K_b \text{ for anion} \quad \text{since } K_a = \frac{K_w}{K_b \text{ for base}}$$

or $K_b \text{ for base} < K_a \text{ for acid}$

$$K_b \text{ for base} = \frac{K_w}{K_a \text{ for acid}}$$

the solution is acidic

example : $\text{NH}_4^+ \text{F}^-$

$$K_a \text{ for } \text{NH}_4^+ = \frac{K_w}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b \text{ for } \text{F}^- = \frac{K_w}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

③ anion hydrolyzes to a greater extent than cation

$$\therefore K_a \text{ for cation} < K_b \text{ for anion}$$

$$K_b \text{ for base} > K_a \text{ for acid}$$

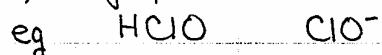
the solution is basic

example : $\text{NH}_4^+ \text{CN}^-$

$$K_a \text{ for } \text{NH}_4^+ = \frac{K_w}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b \text{ for } \text{CN}^- = \frac{K_w}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

Note : For any conjugate acid - base pair



$$K_a \times K_b = K_w$$