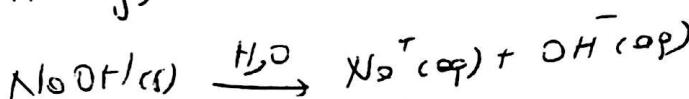
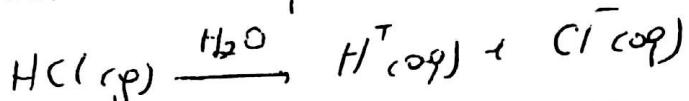


1) Arrhenius Theory:

- An acid is a substance that, when dissolved in water, increases the concentration of H^+ ions.
- A base is a substance that, when dissolved in water, increases the concentration of OH^- ions.

Ex: HCl is an Arrhenius acid. This gas is highly soluble in water and produces H^+ and Cl^- ions.



Arrhenius proposed that in aqueous solutions strong electrolytes (strong acid and base) exist only form of ions.

Whereas weak electrolytes (weak acid or base) exist partly as ions or partly as molecules.

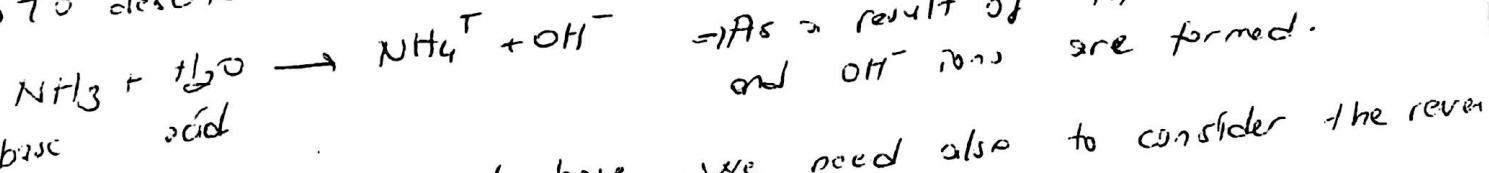
The Arrhenius theory does have limitations. Arrhenius suggest that all bases contain OH^- . Whereas ammonia (NH_3) does not have OH^- but it is a weak base.

2) Brønsted-Lowry Theory of Acids-Bases
Brønsted-Lowry's concept is based on the fact that "acid-base rxns involve the transfer of H^+ ions from one substance to another".

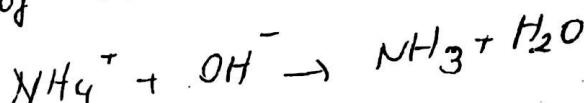
- An acid is a proton donor.

- A base is a proton acceptor.

→ To describe the behaviour of NH_3 as a base, we can write:

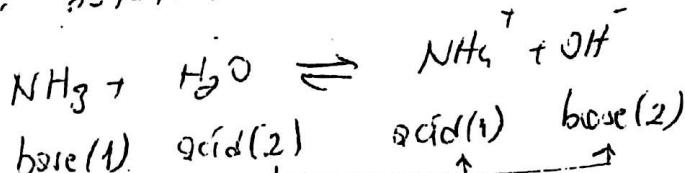


→ Because NH_3 is weak base, we need also to consider the reverse of rxn.



acid base

→ The conventional way to represent a reversible rxn is to use w/ conjugate.



The pair NH_3 / NH_4^+ and the pair H_2O / OH^- in the rxn are referred to as a conjugate acid-base pair.

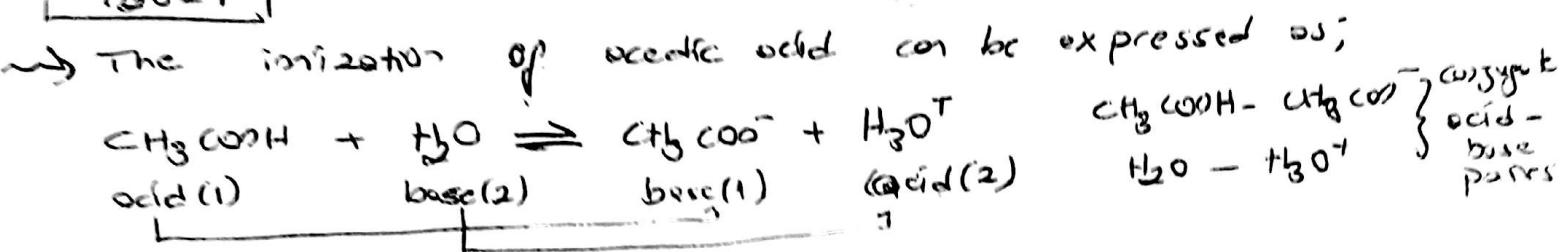
$$K_{a2} = \frac{[NH_3^+][OH^-]}{[NH_3] [H_3O^+]}$$

Water is not written in question.

$$K_{b2} = \frac{[NH_3^+][OH^-]}{[NH_3]}$$

base ionization constant.

$$S + b_0 = 1$$



Ionization of acetic acid can be described in the following way.

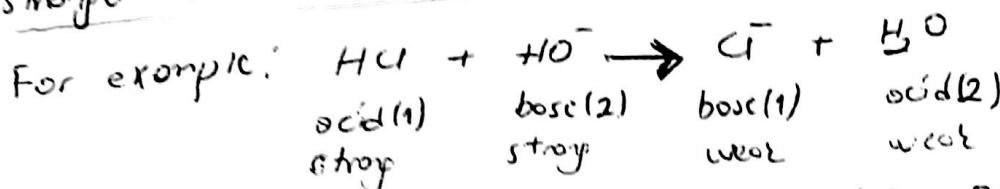
$$K_{a2} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

↓
Acid ionization constant

→ In the first rxn H_2O behaves as an acid and in the second rxn it behaves as a base. If a substance behaves as both an acid and a base it is called amphoteric (amphiprotic).

→ The stronger an acid, the weaker its conjugate base. or.
The stronger a base, the weaker its conjugate acid.

→ In acid-base rxn, the favored direction of the rxn is form the stronger to the weaker member of a conjugate acid-base pair.



Stronger → weaker

Relative Strengths of some common Acid-Base Pairs

ACID

HClO_4	NH_3^+
HI	HCO_3^-
HBr	HPO_4^{2-}
HCl	H_2O
H_2SO_4	CH_3COH
HNO_3	NH_3
H_3O^+	
HSO_4^-	
H_3PO_4	
HF	
HN_3	
CH_3COOH	
H_2CO_3	

BASE

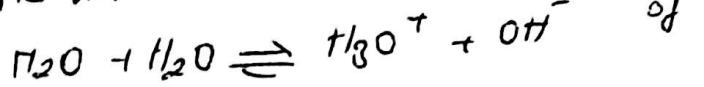
ClO_4^-	NH_3
I^-	CO_3^{2-}
Br^-	PO_4^{3-}
Cl^-	H_2O
HSO_4^-	CH_3O^-
N_3^-	N^{+2}
H_2O	
SO_4^{2-}	
H_2PO_4^-	
F^-	
N_2^-	
CH_3COO^-	
HCO_3^-	

Increasing basic strength

Increasing acid strength

Self-ionization of water and pH scale

One of the most important chemical properties of water is its ability to act as either a base or an acid, depending on the circumstances. In fact, one water molecule can donate a proton to another water molecule. We call this process the self-ionization of water.



Self ionization of water and pH scale.

We can write:

$$K = [H_3O^+] [OH^-] \Rightarrow [H_3O^+] = [OH^-] = 1 \cdot 10^{-7} M \text{ at } 25^\circ C$$

$$K_w = [H_3O^+] [OH^-] = 1 \cdot 10^{-14}$$

Ion product of water or ion-product constant

pH and pOH

The molar concentration of $H^{(aq)}$ and $OH^{(aq)}$ ions in an aqueous solution are usually very small. We therefore usually express $[H^+]$ in terms of pH and $[OH^-]$ in terms of pOH, which is the negative logarithm of $[OH^-]$ or $[-\log [OH^-]]$.

$$pH = -\log [H_3O^+]$$

$$pOH = -\log [OH^-]$$

$$K_w = [H_3O^+] [OH^-] = 1 \cdot 10^{-14}$$

$$-\log K_w = -(\log [H_3O^+] + \log [OH^-]) = -(-14)$$

$$pK_w = pH + pOH = 14$$

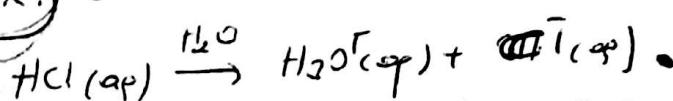
$pH = 7 \Rightarrow$ The solution is neutral

$pH < 7 \rightarrow$ It's acidic

$pH > 7 \rightarrow$ It's basic

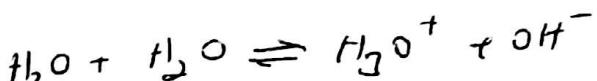
Strong acids and strong bases?

Calculate $[H_3O^+]$, $[Cl^-]$ and $[OH^-]$ ions concentrations in 0.015M $HCl(aq)$



0.015M forms 0.015M $0.015 M$

$$[H_3O^+] = [Cl^-] = 0.015 M$$



All the OH^- ions derived from the self-ionization of water.

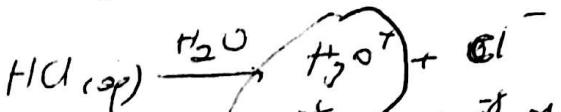
$$K_w = [H_3O^+] [OH^-] = 1 \cdot 10^{-14}$$

$$[OH^-] = 1 \cdot 10^{-14} / 0.015 = \frac{6.7 \cdot 10^{-13}}{0.015} M$$

$$6.7 \cdot 10^{-13} M$$

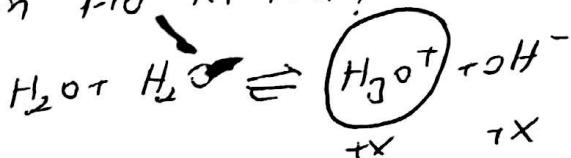
Ex: How to calculate $[H_3O^+]$ in an extremely dilute solution of a strong-acid?

Calculate $[H_3O^+]$, $[OH^-]$, $[Cl^-]$ in $1 \cdot 10^{-8} M HCl$?



$$1 \cdot 10^{-8} M \quad [H_3O^+] = 1 \cdot 10^{-8} M$$

$$[H_3O^+] [OH^-] = (x + 1 \cdot 10^{-8}) x = 10^{-14}$$



$$1 \cdot 10^{-14} = (1 \cdot 10^{-8} + x) \cdot (x)$$

$$x + (1.0 \times 10^{-4} - x) = 1.0 \times 10^{-4}$$

$$x = -\frac{1.0^{-8}}{1.0^{-8} + \sqrt{(10^{-8})^2 - 4 \times 1 \times (-1 \cdot 10^{-14})}} = 3.5 \cdot 10^{-8} \text{ M} = [OH^-]$$

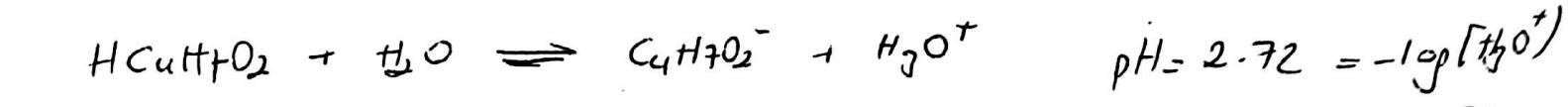
~~! important~~

$[H_3O^+] = 1 \cdot 10^{-8} + 3.5 \cdot 10^{-8} = 1.05 \cdot 10^{-7}$

If the concentration of the acid is 10^{-6} M or less we need to consider H⁺ ions from the self ionization of H₂O.

Weak Acids and Weak Bases:

Ex: A 0.25 M aqueous solution of butyric acid (CH₃CH₂CO₂H) is found to have a pH of 2.72. Determine K_a for butyric acid?



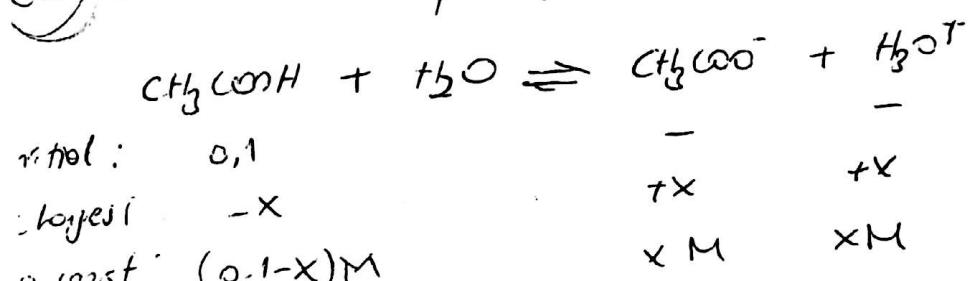
initial:	0.25 M	-	-
react:	-	+x	+x
after:	-x M	x M	x M
p-const:	(0.25-x) M		

$$[H_3O^+] = 10^{-2.72}$$

$$\frac{[H_3O^+]^2}{[H_3O^+] \cdot (1.8 \cdot 10^{-3})} = x$$

$$K_a = \frac{x \cdot x}{0.25 - x} = \frac{(1.8 \cdot 10^{-3})^2}{0.25 - 1.8 \cdot 10^{-3}} = 1.5 \cdot 10^{-5} \quad K_a > K_w$$

What is the pH of 0.1 M acetic acid solution? ($K_a = 1.8 \cdot 10^{-5}$)



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.8 \cdot 10^{-5} = \frac{x^2}{0.1 - x}$$

\downarrow neglecting x

$$x^2 = 1.8 \cdot 10^{-5}$$

$$x = 1.3 \cdot 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(1.3 \cdot 10^{-3}) = \underline{\underline{2.88}}$$

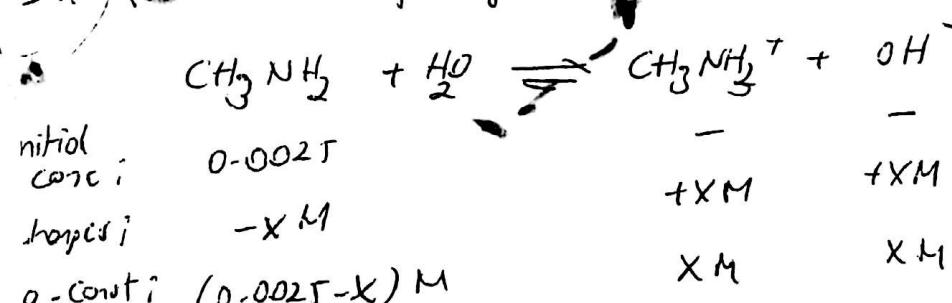
Now, we must check our assumption:

$$M - x \approx M \quad \text{so}$$

$$0.1 - 0.0013 \approx 0.098 \approx 0.1$$

Our assumption is good, ($\% 1$ hate margin of error)

Ex: What is the pH of solution that is 0.0025 M CH₃NH₂(aq)? $K_b = 4.2 \cdot 10^{-4}$



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

$$4.2 \cdot 10^{-4} = \frac{x^2}{0.0025 - x}$$

\downarrow ignore x

$$x = 4 \cdot 2 \cdot 10^{-5}$$

$$x = [OH^-] = 4 \cdot 10^{-5} M$$

too large to ignore $M-x = 0.0025 - 0.001 = 0.0015$

$$\frac{0.001}{0.0025} \cdot 100\% = 40\%$$

Our assumption failed, so we must use the exact method.

$$\frac{x^2}{0.0025-x} = 4 \cdot 10^{-5}$$

$$x^2 + (4 \cdot 10^{-5}x) - (1 \cdot 1 \cdot 10^{-6}) = 0$$

$$x = \frac{(-4 \cdot 10^{-5}) \pm \sqrt{(4 \cdot 10^{-5})^2 + 4 \times 1 \cdot 10^{-6}}}{2}$$

$$x = [OH^-] = 8 \cdot 4 \cdot 10^{-5} M$$

$$pOH = 2.08$$

$$pH = 10.9$$

Simplifying Assumption:

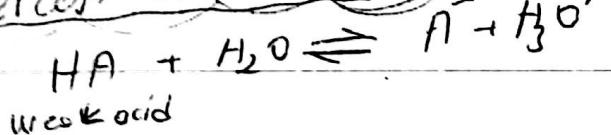
In general, the assumption works if the ratio of the molarity of weak acid MA or weak base MB to the K_a or K_b is greater than 100.

$$\frac{MA \text{ (or } MB)}{K_a \text{ (or } K_b)} > 100$$

To check the validity of assumption, we have to find the value less than 5%.

$$\frac{[H_3O^+] \text{ or } [OH^-]}{[\text{weak acid}] \text{ or } [\text{weak base}]} \times 100 < 5\%$$

Percent Ionization:



Weak acid

for the ionization of HA, percent ionization gives the proportion of ionized molecules on a percentage basis.

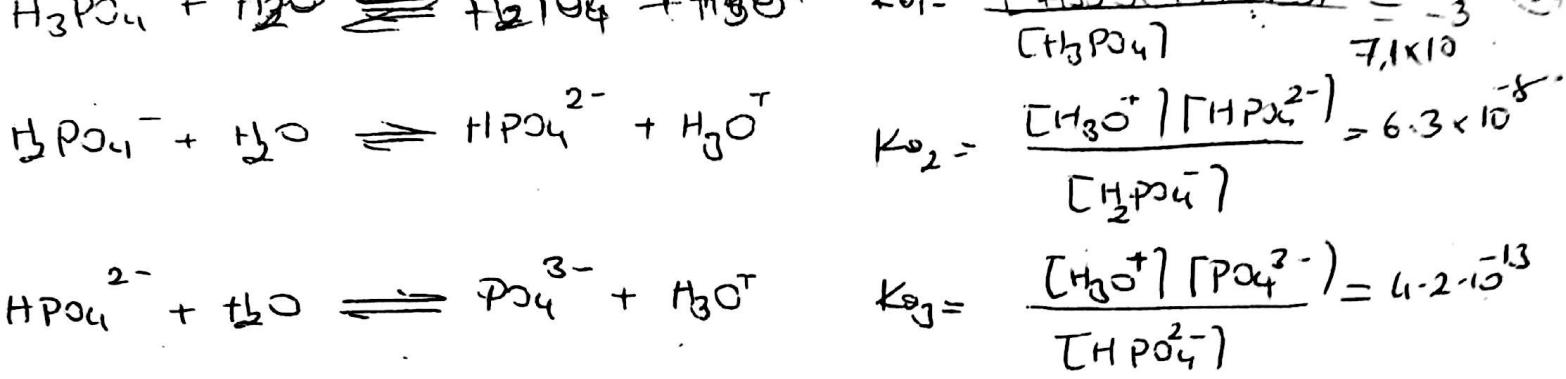
$$\text{Percent ionization} = \frac{\text{molarity of } H_3O^+ \text{ derived from HA}}{\text{initial molarity of HA}} \times 100$$

The percent ionization of weak acid or a weak base increases as the solution becomes more dilute.

POLYPROTIC ACIDS:

Many acids have more than one ionizable H atom. These acids are known as polyprotic acids.

(1) Phosphoric Acid: The H_3PO_4 has three ionizable H atoms; it is a triprotic acid. It ionizes in 3 steps. For each step, we can write an ionization equation and a ionization constant.



$$K_{\text{a}_1} > K_{\text{a}_2} > K_{\text{a}_3}$$

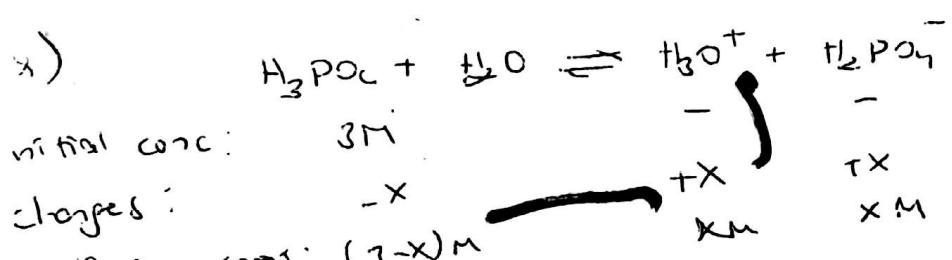
Ionization will be more difficult from 1 step to 3 step. Because it is difficult to take away a proton from negative ion.

~~We can make 3 key statements:~~

- 1) K_{a_1} is so much larger than K_{a_2} and K_{a_3} that all H_3O^+ is produced in the first ionization step.
- 2) So little of the H_2PO_4^- forming in the first ionization step ionizes any further that we can assume $[\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+]$
- 3) $[\text{HPO}_4^{2-}] \approx K_{\text{a}_2}$, regardless of the molarity of the acid.

~~For a 3 M H_3PO_4 solution, calculate $[\text{H}_3\text{O}^+]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, $[\text{PO}_4^{3-}]$.~~

Solution: Because K_{a_1} is so much larger than K_{a_2} , let's assume that all the H_3O^+ forms in the first ionization.



$$K_{\text{a}_1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.1 \cdot 10^{-3} = \frac{x^2}{3-x}$$

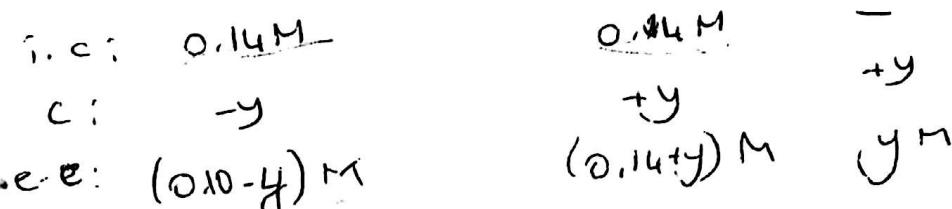
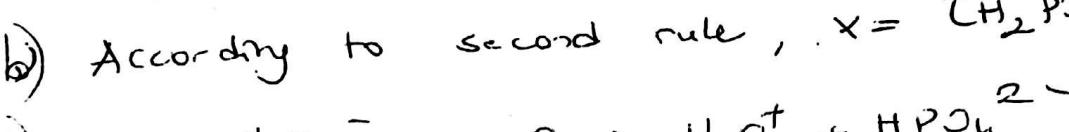
is very near

In the assumption:

$$3.0 - 0.14 = 2.86 \approx 0.3$$

0.14 ± 0.04 (margin of error or tolerance)

$$x = [\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+] = 0.14 \text{ M}$$

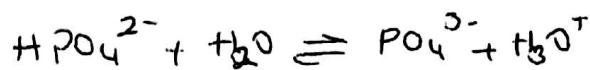


$$K_{\text{O}_2} = \frac{(\text{H}_3\text{O}^+) [\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(0.14y) \cdot y}{0.14y} = 6.3 \cdot 10^{-5} \quad (4)$$

$$y = [\text{HPO}_4^{2-}] = K_{\text{O}_2} \cdot 6.3 \cdot 10^{-5}$$

According to this result the assumption is valid.

The PO_4^{3-} ion forms only in the 3rd step of ionization.



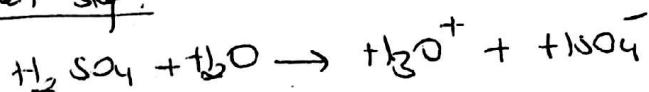
$$K_{\text{O}_3} = \frac{[\text{PO}_4^{3-}] [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = \frac{[\text{PO}_4^{3-}] \cdot 0.14}{6.3 \cdot 10^{-5}} = 4.2 \cdot 10^{-13} \Rightarrow [\text{PO}_4^{3-}] = \frac{1.9 \cdot 10^{-19}}{1.9 \times 10^{-13}}$$

SULFURIC ACID (H_2SO_4)

- H_2SO_4 is a strong acid in its first ionization and a weak in its second.
- Ionization is complete in the first step, which means that in most H_2SO_4 (aq) solutions $[\text{H}_2\text{SO}_4] \approx 0$.

Ex: Calculate $[\text{H}_3\text{O}^+]$, $[\text{HSO}_4^-]$, $[\text{SO}_4^{2-}]$ in 0.5 M H_2SO_4

1. ionization step:



Init. conc:	0.5 M	-	-
changes:	-0.5 M	+0.5	+0.5
eq. concs:	≈ 0	0.5 M	0.5 M

2nd ionization step



in. c:	0.5 M	-	-
c:	-x M	+x M	+x M
e.c:	$0.5 - x$	(0.5 + x)	x

$$K_{\text{O}_2} = \frac{[\text{H}_3\text{O}^+] [\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.1 \cdot 10^{-2}$$

$$\frac{(0.5 + x)(x)}{0.5 - x} = 1.1 \cdot 10^{-2}$$

$$x = [\text{SO}_4^{2-}] = 1.1 \cdot 10^{-2}$$

If we assume x is much smaller than 0.5,
then $0.5 + x \approx 0.5 - x \approx 0.5$

our results are:

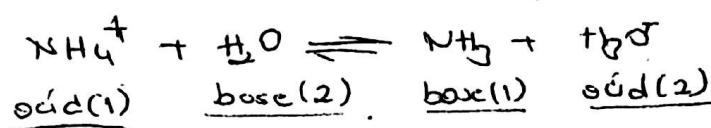
$$[\text{H}_3\text{O}^+] = 0.5 + x = 0.5 + 1.1 \cdot 10^{-2} = 0.51 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.011 \text{ M}$$

$$[\text{HSO}_4^-] = 0.5 - x = 0.49 \text{ M}$$

IONS AS ACIDS and BASES:

- Ions can act as acids or bases. For instance, in the second ionization steps of a polyprotic acid, an anion acts as an acid.
- Let's think about the ionization of NH_4^+ ion:



Equilibrium of this rxn is described by acid ionization constants

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

- we know the ionization rxn of NH_3 :



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

$$\Rightarrow K_a \times K_b = ?$$

$$\frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$(K_a \times K_b = [\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w) \blacksquare \blacksquare \blacksquare !$$

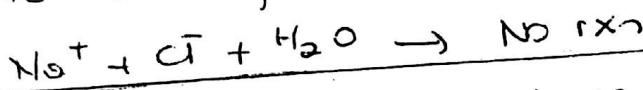
- The product of the ionization constants of an acid and its conjugate base equals the ion product of water.

$$K_a (\text{acid}) \times K_b (\text{its conjugate base}) = K_w \quad \text{Similarly}$$

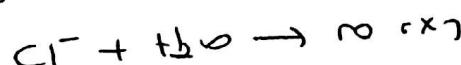
$$K_b (\text{base}) \times K_a (\text{its conjugate acid}) = K_w$$

HYDROLYSIS:

- When NaCl dissolves in water, complete dissociation into Na^+ and Cl^- ions occurs, and the pH of solution remains 7.00.
- We can represent this fact with the equation:

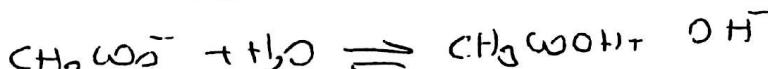
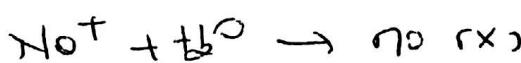


- When NH_4Cl is added to water, the pH falls below 7.
- This means that $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ in solution. A rxn products H_3O^+ ions.



A rxn between an ion and water is often called a hydrolysis rxn.
We can say that Cl^- ion does not hydrolyze but NH_4^+ ion hydrolyzes

- When sodium acetate is dissolved in water, the pH rises above 7. This means that $[\text{OH}^-] > [\text{H}_3\text{O}^+]$.



Na^+ ion → does not hydrolyze
 $\text{Acetate ion} \rightarrow$ hydrolyzed

The pH of salt solutions

i) Salts of strong acids and strong bases (NaCl) do not hydrolyze;

The pH of solution = 7

ii) Salts of strong bases with weak acids (CH_3COONa) hydrolyze:
 $\text{pH} > 7$ (The anion acts as a base) $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$

iii) Salts of weak bases and strong acids (NH_4Cl) hydrolyze; $\text{pH} < 7$
(The cation acts as an acid) - $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$

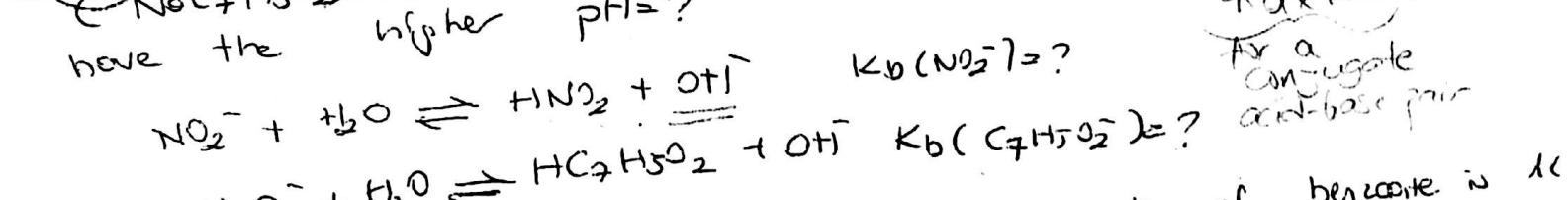
iv) Salts of weak bases and weak acids ($\text{NH}_4\text{CH}_3\text{COO}$) hydrolyze;
The cations are acids and anions are bases, whether the solution
is acidic or basic, depends on the values of K_a and K_b .

Ex: Predict whether each of the following solutions is acidic,
basic or neutral. a) NaOCl(aq) ; b) KCl(aq) ; c) $\text{NH}_4\text{NO}_3(\text{aq})$

a) Na^+ does not hydrolyze $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$ (OCl^- hydrolyzes and forms basic soln)
 $\text{pH} = 7$

b) Neither K^+ nor Cl^- hydrolyze. KCl(aq) is neutral

c) NO_3^- does not hydrolyze
 NH_4^+ hydrolyzes and the solution is acidic.
Ex: If solution of sodium nitrate (NaNO_3) and sodium benzoate
($\text{NaC}_7\text{H}_5\text{O}_2$) have the same molarity, which solution will
have the higher pH?



$$K_b(\text{C}_7\text{H}_5\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_7\text{H}_5\text{O}_2 + \text{OH}^- \quad K_b(\text{C}_7\text{H}_5\text{O}_2^-) = ?$$

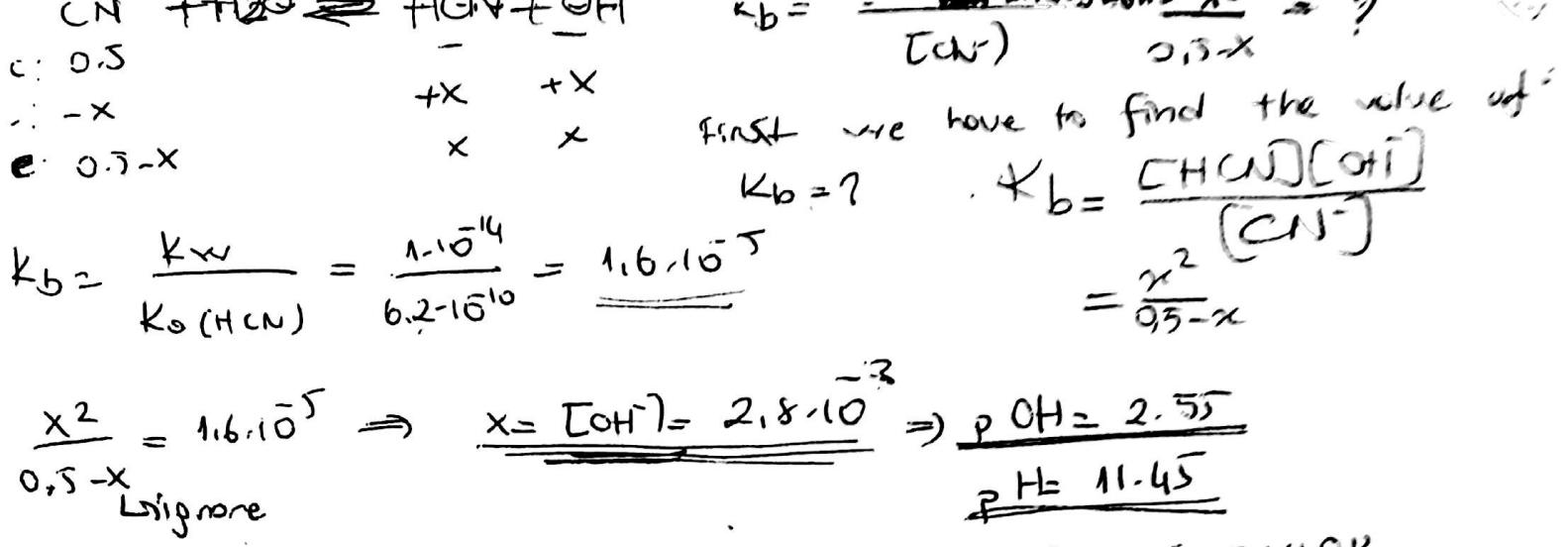
$$K_b(\text{NO}_3^-) = \frac{K_w}{K_a(\text{HNO}_2)} = \frac{1 \cdot 10^{-14}}{7.12 \cdot 10^{-4}} = 1.4 \cdot 10^{-11}$$

$$K_b(\text{C}_7\text{H}_5\text{O}_2^-) = \frac{K_w}{K_a(\text{HC}_7\text{H}_5\text{O}_2)} = \frac{1 \cdot 10^{-14}}{6.3 \cdot 10^{-5}} = 1.6 \cdot 10^{-10}$$

more basic

The K_b of benzoate is 11 times higher than the K_b of NO_3^- . The benzoate ion hydrolyzes more and gives a higher amount of OH^- . A sodium benzoate solution is more basic & have a higher pH.

Ex: Are NaCN(aq) sodium cyanide solutions normally acidic/basic
pH neutral? What is the pH of 0.5 M NaCN(aq) ?
 Na^+ does not hydrolyze



MOLECULAR STRUCTURE and ACID-BASE BEHAVIOR

Strengths of Binary Acids: weak, $\star \left\{ \begin{array}{l} \text{In general the stronger} \\ \text{H-X bond, the weaker} \\ \text{the acid is.} \end{array} \right.$

$H_I \quad HBr \quad HCl \quad HF$
 1st length: $160 > 141 > 127 > 91$. shorter, stronger H-X bond; weaker acid.
 2nd class: $287 < 368 < 431 < 569 \text{ kJ/mol}$

Strong bond is characterized by short bond lengths and high-bond dissociation energies.

$K_a = \frac{HI}{10^9} > \frac{HBr}{10^8} > \frac{HCl}{1.3 \cdot 10^6} > \frac{HF}{6.6 \cdot 10^4}$
 strong
weaker
stronger the acid, the bigger the K_a .

HF is a weaker acid than other hydrogen halides, because of the hydrogen bonding in HF.

$HF + H_2O \rightarrow (F \cdots H_2O) \rightleftharpoons H_3O^+ + F^-$
 ion-pair

Ion-pairs are held together by strong hydrogen bonds and decrease the free H_3O^+ concentration

$X: \quad CH_4 \quad NH_3 \quad H_2O \quad HF$
 $\Delta EN: \quad 0.4 < 0.9 < 1.4 < 1.9$

IN A PERIOD: the strengths of binary acids within a period bond polarity must be dominant factor. As the acid strength increases, the polarizability of the bond increases. The greater the electronegativity difference (ΔEN) in the bond H-X, the more polar is the bond. Thus, the loss of H^+ more readily from a polar bond.

so CH_4 and NH_3 have no acidic properties in water, and the acidity of H_2O is very limited.

WHEN COMPARING BINARY ACIDS IN THE SAME GROUP OF PERIODIC TABLE: acid strength increases as the length of the bond increases.

IN A GROUP: acid strength \uparrow , as the bond length \uparrow .

2) Strengths of Oxides

- We must focus on the attraction of \bar{e} s from the O-H bond toward the central atom. The following factors are important in this \bar{e} withdrawal:

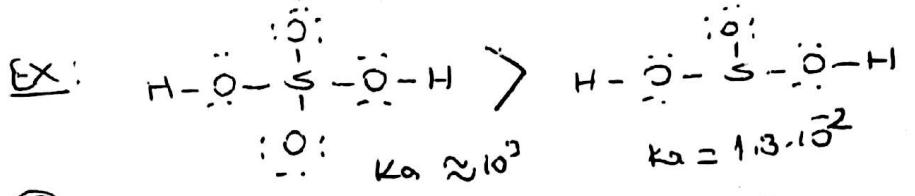
1) a high electronegativity of the central atom

2) a large number of terminal O atoms in the acid molecule



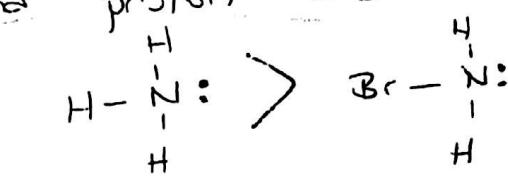
$$EN_{Cl} = 3$$

$$EN_{Br} = 2.8$$



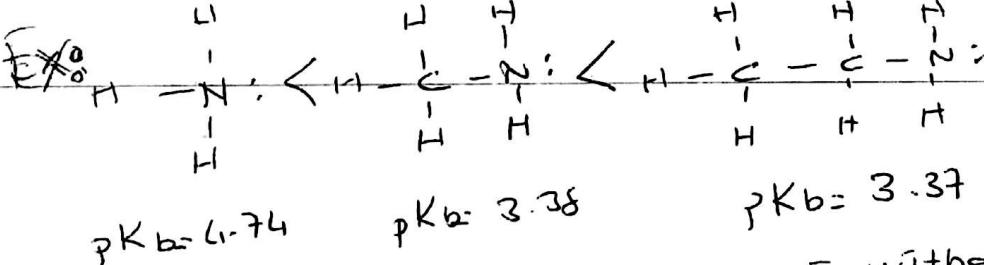
(3) Strengths of Amines as Bases

Amine molecules have lone-pair \bar{e} s, and the lone-pair \bar{e} s bind proton and act as a base.



ammonia bromine
decreases the ability to bind H as lone pairs are attracted by Br \Rightarrow base is weaker.

The electronegativity of Br atom is higher than H atom. This Br atom withdraws \bar{e} density from the N atom. The lone-pair \bar{e} s cannot bind a proton as strongly, and bind a proton as strongly, and



CH chains do not withdraw \bar{e} s, so the base is stronger.

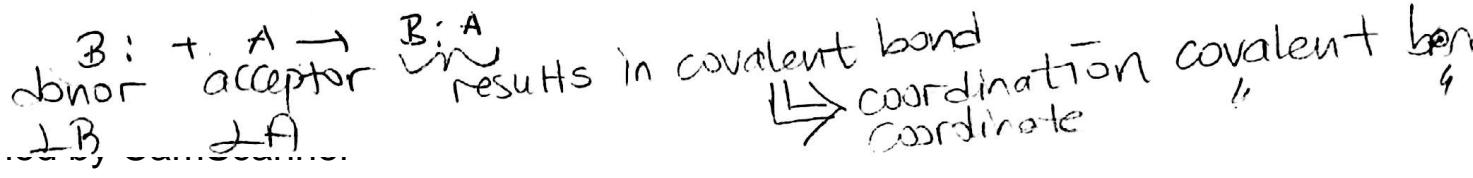
Hydrocarbon chains have no \bar{e} -withdrawing ability but they have \bar{e} donating ability and a base is stronger.

(4) Lewis Acids and Bases

- A Lewis acid is an \bar{e} -pair acceptor

- A Lewis base " " " donor

- rxn between a Lewis acid (A) and Lewis base (B) results in the formation of covalent bond between them. The name of this bond is "coordination" or "coordinate covalent bond".



$\xrightarrow{\text{coordination covalent bond}}$
coordinate

