CHM 1220-Dang Chapter 16 – Aqueous Equilibria: Acids and Bases

Properties of Acid

- Sour taste
- Ability to dissolve many metals
- Ability to neutralize bases
- Change blue litmus paper to red

Properties of Base

- Taste bitter

alkaloids = plant product that is alkaline often poisonous

- Feel slippery
- Ability to turn red litmus paper blue
- Ability to neutralize acids

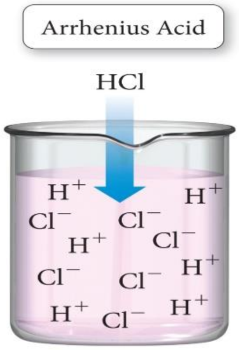
Definition of Arrhenius acids and bases

Acid: any compounds that produce H^+ when dissolve in water

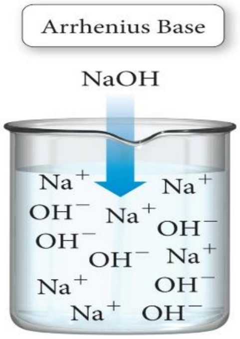
$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

Base: any compounds that produce ^-OH when dissolve in water

$$MOH_{(aq)} \rightleftharpoons M^+_{(aq)} + {}^-OH_{(aq)}$$



$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$



$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

Problems:

- It does not explain why molecular substances, such as NH_3, dissolve in water to form basic solutions, even though they do not contain ^-OH ions.
- It does not explain how some ionic compounds, such as Na_2CO_3 or Na_2O, dissolve in water to form basic solutions, even though they do not contain ^-OH ions.
- It does not explain why molecular substances, such as CO_2, dissolve in water to form acidic solutions, even though they do not contain H^+ ions.
- It does not explain acid–base reactions that take place outside aqueous solution.

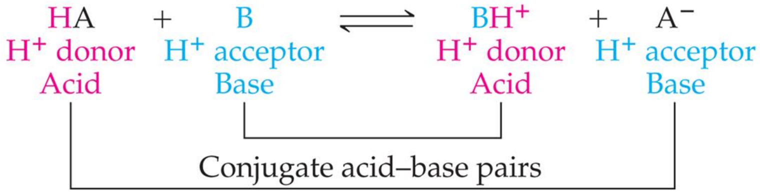
This theory is limited to only "those compounds"

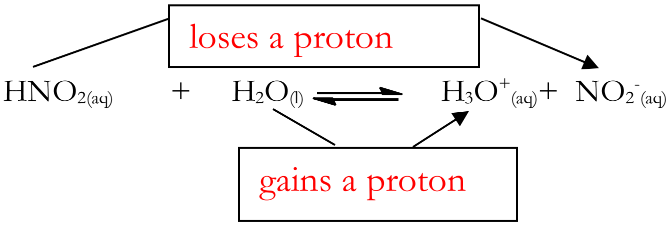
16.1 The Brønsted-Lowry Theory:

- a better definition for acids and bases in aqueous solution

Brønsted-Lowry Acid: A substance that can transfer hydrogen ions, H^+. In other words, a proton donor

Brønsted-Lowry Base: A substance that can accept hydrogen ions, H^+. In other words, a proton acceptor





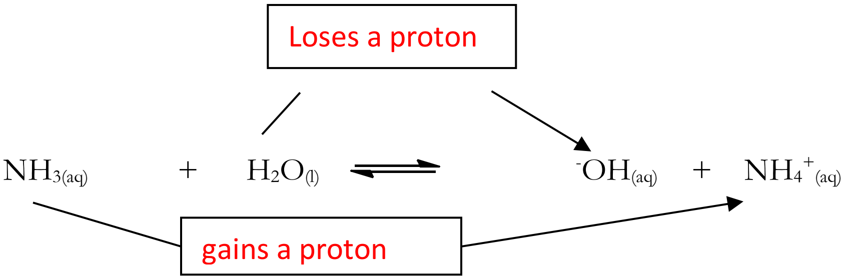
$HNO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_2^-{}_{(aq)}$

Conjugate Acid-Base Pairs: Chemical species whose formulas differ only by one hydrogen ion, H^+

HNO_2 and NO_2^-

H_2O and H_3O^+

In the acid example, notice the formation of H_3O^+ -- this species is named the hydronium ion. It lets you know that the solution is acidic!



$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons {}^-OH_{(aq)} + NH_4^+{}_{(aq)}$

Conjugate Acid-Base pairs

NH_3 and NH_4^+

H_2O and ^-OH

Amphoteric Substances -Hydrated Protons and Hydronium Io

- Amphoteric substances can act as either an acid or a base because they have both a transferable H^+ and an atom with lone pair electrons.
- Water acts as base, accepting H^+ from HCl.

$HCl_{(aq)} + H_2O_{(l)} \rightarrow Cl^-{}_{(aq)} + H_3O^+{}_{(aq)}$

- Water acts as acid, donating H^+ to NH_3.

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + {}^-OH_{(aq)}$

Due to high reactivity of the hydrogen ion, it is actually hydrated by one or more water molecules.

$$[H(H_2O)_n]^+ \begin{cases} n = 1 & H_3O^+ \\ n = 2 & H_5O_2^+ \\ n = 3 & H_7O_3^+ \\ n = 4 & H_9O_4^+ \end{cases}$$

For our purposes, H^+ is equivalent to H_3O^+.

Examples: Write a balanced equation for the dissociation of each of the following Bronsted-Lowry acids in water

$H_2CO_{3(aq)}$

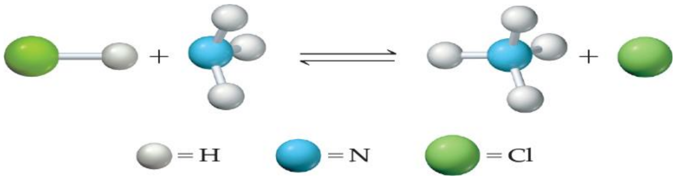
$HSO_4^-{}_{(aq)}$

Examples: Write a balanced equation for the dissociation of each of the following Bronsted-Lowry bases in water

$CO_3^{2-}{}_{(aq)}$

$CH_3NH_{2(aq)}$

Consider the given reaction and choose the best answer:



A. Conj. acid – base pair 1: HCl (acid) and NH_3 (base)
   Conj. acid – base pair 2: NH_4^+ (acid) and Cl^- (base)
B. Conj. acid – base pair 1: HCl (acid) and Cl^- (base)
   Conj. acid – base pair 2: NH_3 (base) and NH_4^+ (acid)
C. Conj. acid – base pair 1: HCl (acid) and Cl^- (base)
   Conj. acid – base pair 2: NH_3 (acid) and NH_4^+ (base)

16.2 Acid Strength and Base Strength

Acid-dissociation equilibrium helps to realize that the two bases, H_2O and A^- are competing for protons:

$$\underset{\text{Acid}}{HA(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Acid}}{H_3O^+(aq)} + \underset{\text{Base}}{A^-(aq)}$$

With equal concentrations of reactants and products, what will be the direction of reaction?

If H_2O is a stronger base (stronger H^+ acceptor) than A^-, the majority of protons will be transferred from HA to H_2O and the solution will contain mainly H_3O^+ and A^-

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Solution contains mainly products when H_2O is a stronger base than A^-.

If A^- is a stronger base than H_2O, the ions will get the protons, and the solution will contain mainly HA and H_2O.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Solution contains mainly reactants when A^- is a stronger base than H_2O.

When beginning with equal concentrations of reactants and products, the protons is always transferred to the stronger base. This means that the direction of reaction to reach equilibrium is proton transfer from the stronger acid to the stronger base to give weaker acid and weaker base:

Stronger acid + stronger base → Weaker acid + Weaker base

Recall:

Strong acids: $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

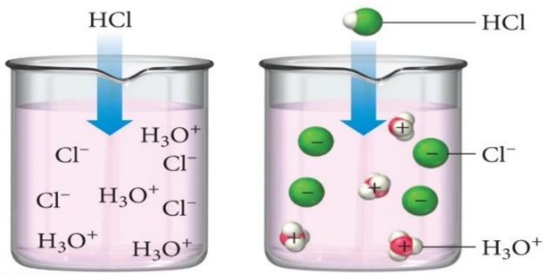
Strong acids donate practically all their H's.

100% ionized in water (strong electrolytes)

$[HA]_{ini} = [H_3O^+]$

A Strong Acid

When HCl dissolves in water, it ionizes completely.



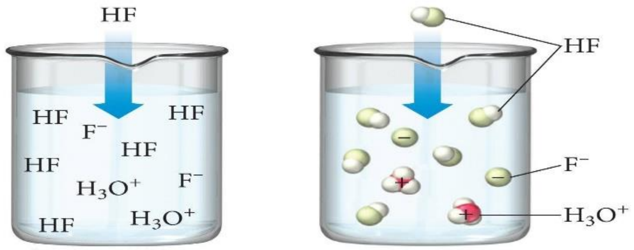
6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

- **Other acids are considered weaker acids or "weaker acids"**

$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.



Weak acids donate a small fraction of their H's.

Most of the weak acid molecules do not donate H to water.

Much less than 1% ionized in water

$[H_3O^+] << [\text{weak acid}]$

Strong bases:

- Completely ionized in water to produce ^-OH

- $[MOH]_{ini} = [^-OH]$

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + {}^-OH_{(aq)}$

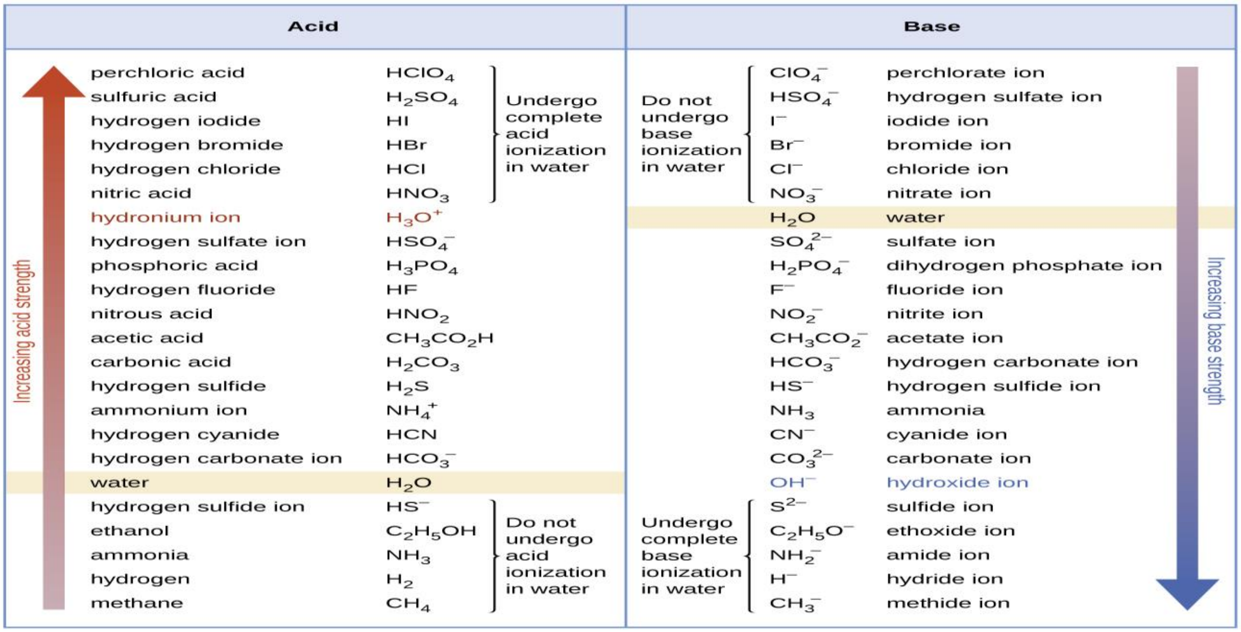
Weak Bases:

- dissociate only to a slight extent in water
- only a small percentage of the base molecules form ^-OH ions, either through dissociation or reaction with water

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons {}^-OH_{(aq)} + NH_4{}^+_{(aq)}$

The inverse relationship between the strength of an acid and the strength of its conjugate base is shown in the table below:

- The stronger an acid is at donating H, the weaker the conjugate base is at accepting H.



Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			NH_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Example: If you mix equal amount concentrations of reactants and products, decide which species (reactants or products) are favored at the completion of the reaction. Why?

$H_2SO_{4(aq)} + NH_{3(aq)} \rightleftharpoons NH_4{}^+_{(aq)} + HSO_4{}^-_{(aq)}$

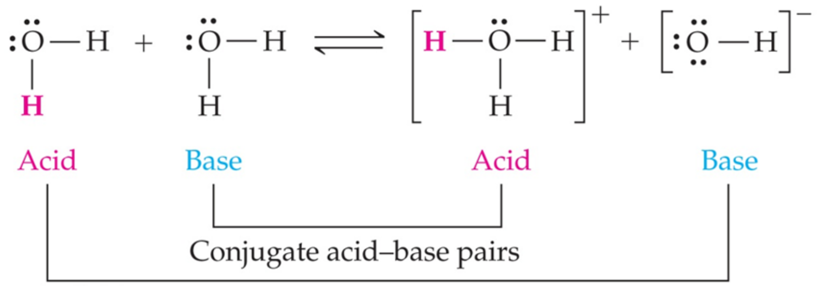
$HF_{(aq)} + NO_3^-{}_{(aq)} \rightleftharpoons HNO_{3(aq)} + F^-{}_{(aq)}$

16.4 Dissociation of Water : Autoionization of water

Fredrich Kohlrausch, around 1900, found that no matter how pure water is, it still conducts a minute amount of electric current. This proves that water self-ionizes.

- Since the water molecule is amphoteric, it may dissociate with itself to a slight extent.
- *Only about 2 in a billion water molecules are ionized at any instant!*

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$



At 25°C **$[H_3O^+] = [^-OH] = 1.0 \times 10^{-7}$ M**

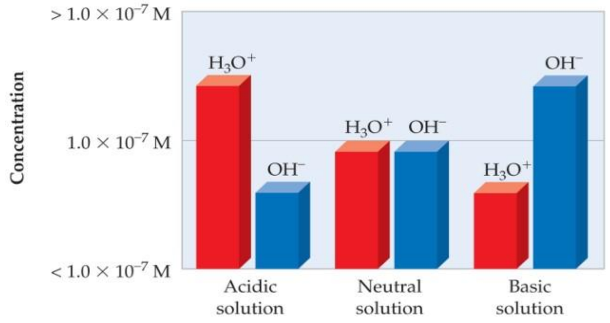
The equilibrium expression used here is referred to as the **autoionization constant for water, K_w**

$$K_w = [H_3O^+]\,[^-OH] = 1.0 \times 10^{-14}$$

Knowing this value will help to calculate $[H_3O^+]$ or $[^-OH]$ at various situations

Knowing this value will help to calculate $[H_3O^+]$ or $[^-OH]$ at various situations

Dissociation of Water (3 of 4)



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Acidic: $[H_3O^+] > [^-OH]$

Basic: $[H_3O^+] < [^-OH]$

Neutral: $[H_3O^+] = [^-OH]$

Example: At 60°C, the value of K_w is 1.0×10^{-13}. Calculate the $[H_3O^+]$ and $[^-OH]$ in a neutral solution then explain the effect of changing temperature.

16.5 The pH Scale and Significant figures

Used to designate the $[H^+]$ in most aqueous solutions where $[H^+]$ is small.

$pH = -\log [H^+]$ **$pOH = -\log [^-OH]$** **$pH + pOH = 14.00$**

Acidic: $pH < 7.00$	**Neutral: $pH = 7.00$**	**Basic: $pH > 7.00$**

The hydronium ion concentration for lemon juice is approximately 0.0025 M. What is the pH when $[H_3O^+]$ = 0.0025 M?

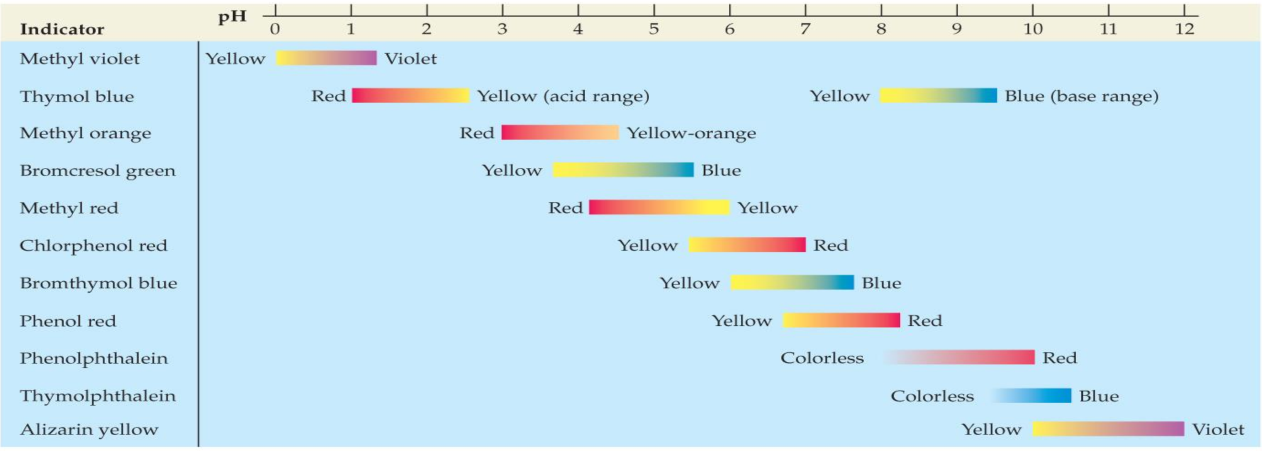
$$pH = -\log(0.00\overbrace{25}^{\text{2 significant figures}}) = 2.\underbrace{60}_{\text{2 decimal places}}$$

Example: Calculate the $[^-OH]$ in a solution with $[H_3O^+] = 7.5 \times 10^{-5}M$. Is this solution basic, acidic or neutral?

Calculate the concentration of H_3O^+ and ^-OH for a solution with a pH of 8.37

16.6 Measuring pH

The approximate pH of a solution can be determined by using acid-base indicator, a substance that changes color in specific pH range.



$$HIn(aq) \quad + \quad H_2O(l) \rightleftharpoons \quad In^{-}(aq) \quad + \quad H_3O^{+}(aq)$$

acid **base**

color A color B

The acid and its conjugate base have different colors. At low pH, the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has the color A. At high pH, the concentration of H_3O^+ is low and so the equilibrium position thus lies to the right and the equilibrium solution has color

More accurate pH values can be determined with an electronic instrument called a pH meter, a device that measures the pH-dependent electrical potential of the test solution.