Lecture 36
Aqueous Equilibria

$\rightleftharpoons$

This is all about: reactions/equilibria in water.

Water is special. why?

Large dipole moment

Very good hydrogen bonding

Very strong intermolecular interactions with itself

So what?

Large dipole moment, allows it to *dissolve ions*

Hydrogen bonding allows it to dissolve H-bonding species (alcohols, acetic acid, etc.).

Unique solvent

Lecture 36 Aqueous Equilibria

Remember:

2 kinds of species:

- Electrolyte (makes ions)
  - strong
    - totally dissociated into ions
  - weak
    - very little dissociation into ions

- Nonelectrolyte
  - No ionization at all.

Strong electrolytes

How do you know if it is a strong electrolyte?

- It has to be one of these:
  - A salt (that dissolves)
    - Examples: $NaCl$, $MgBr_2$, Na_2SO_4
  - The strong acids:
    - HCl, HBr, HI $HClO_4$, HNO_3, H_2SO_4
  - Strong base:
    - Group 1 or II hydroxide salts:
    - Examples: $NaOH$, $Mg(OH)_2$, $LiOH$…
- Nonelectrolyte
  - No ionization at all.

Strong electrolytes

An aside:

Debye Huckel:

Complete ionization is an approximation

There are always some non-ionized

Example: I < 2 for NaCl (only slightly)

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Weak electrolytes

What is a weak electrolyte?

Weak acid (every acid that's not a strong acid)

Examples: CH_3COOH, HNO_2, HF, HCN

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

Weak bases (every other base)

Example: NH_3

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

system lies very far toward reactants

K (equilibrium constant very small 4×10^{-10})

concentrations of products very small.

Weak electrolytes ionic equations

Since weak electrolytes don't completely dissociate:

In an ionic equation, write them as not dissociated:

$$HCN + NaOH \rightleftharpoons NaCN + H_2O$$

$$HCN + Na^+ + OH^- \rightleftharpoons Na^+ + CN^- + H_2O$$

$$HCN + OH^- \rightleftharpoons CN^- + H_2O$$

$$HCl + NH_3 \rightleftharpoons NH_4Cl$$

$$H^+ + Cl^- + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

Definition of an acid:

Previously: defined an acid as increasing H^+

Actually 3 ways to define acid/base:

Arrhenius (specific to water)

Bronsted Lowry (most useful and clear)

Lewis (most general definition)

1. Arrenius (aqueous only)
    1. Acid: increases the $[H_3O^+]$ (concentration)
    2. Base: increases the $[OH^-]$ (concentration)
    3. Example: HCl

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Neutralization: $H_3O^+ + OH^- \longrightarrow 2H_2O$

Definition of an acid:

2. Bronsted Lowry (most useful)
   1. Acid: A substance that donates an H^+
   2. Base: A substance that accepts an bH^+
   3. Example;

Base acid acid base

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

Weaker stronger

2 conjugate acid/base pairs
Acid/base pair, differs by 1 H^+
Equilibrium always lies on the weaker side.

Definition of an acid:

2. Bronsted Lowry (most useful)
   2. Another example;

Base acid acid base

$$\underset{\text{Base}}{CH_3CO_2^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{CH_3CO_2H} + \underset{\text{base}}{OH^-}$$

Weaker stronger

The equation represents the hydrolysis of the acetate ion in aqueous solution to produce a basic solution.

What is hydrolysis (*hydro* water, *lysis* cut)

$\longrightarrow$

$\longrightarrow$

Definition of an acid:

3. Lewis (most general, does not even need H^+)

    Acid: a substance that accepts and electron pair

    Base: a substance that donates an electron pair

The reaction between an acid and a base is the donation of a pair of electrons from the base to the acid and the formation of a coordinate bond.

$H^+ \leftarrow :OH^- \longrightarrow H_2O$

$F_3B \leftarrow :NH_3 \longrightarrow F_3B\text{-}NH_3$

Lecture 37: Brondsted-Lowry acid-base equlibrium

To reiterate: Must recognize: strong acid, strong base, weak acid, weak base and a salt.

Examples:

HNO_3	NH_4ClO_4
KOH	$KClO$
KCN	CH_3CO_2H
$NaHCO_3$	HF
$CaSO_3$	H_3PO_4
NH_3	

Lecture 37: Brondsted-Lowry acid-base equlibrium

To reiterate: Must recognize: strong acid, strong base, weak acid, weak base and a salt.

Examples:

HNO_3	acid, strong	NH_4ClO_4	acid, weak
KOH	base, strong	KClO	base, weak
KCN	base, weak	CH_3CO_2H	acid, weak
$NaHCO_3$	base, weak	HF	acid, weak
$CaSO_3$	base, weak	H_3PO_4	acid, weak
NH_3	base, weak	NH_4F	acid, weak

Lecture 37: Brondsted-Lowry acid-base equlibrium

In every Bronsted-Lowry equilibrium:

each acid has a conjugate base

each base has a conjugate acid.

difference between acid & conjugate base is one H^+.

More Examples:

Acid	Base
H_2SO_3	HSO_3^-
HCN	CN^-
$H_2PO_4^-$	HPO_4^{2-}
H_2CO_3	HCO_3^-
HCO_3^-	CO_3^{2-}

B.-L. acid-base equlibrium

It is instructive to list acids & bases in order of strength

Acid	Base	
$HClO_4$	ClO_4^-	
HNO_3	NO_3^-	
H_3O^+	H_2O	H_3O^+, strngest acid in H_2O
H_3PO_4	$H_2PO_4^-$	
H_2SO_3	HSO_3^-	
CH_3CO_2H	$CH_3CO_2^-$	
H_2CO_3	HCO_3^-	
NH_4^+	NH_3	
H_2O	OH^-	OH^- strongest base in H_2O
NH_3	NH_2^-	

B.-L. acid-base equlibrium

Any acid stronger than water:

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$

both strong acids $\longrightarrow$ both produce same H_3O^+

Base stronger than OH^-

$NH_2^- + H_2O \quad OH^- + NH_3$

Any acid/base stronger just gets completely converted into H_3O^+ or OH^-.

Strong acid: any acid stronger than H_3O^+

Weak acid: any acid weaker than H_3O^+

Hydrogen ion concentration & pH

$[H_3O^+]$ 1M-----------------10^{-7}M--------------------10^{-14}M

strong acid   neutral   strongly base

pH   0-------------------7------------------------14

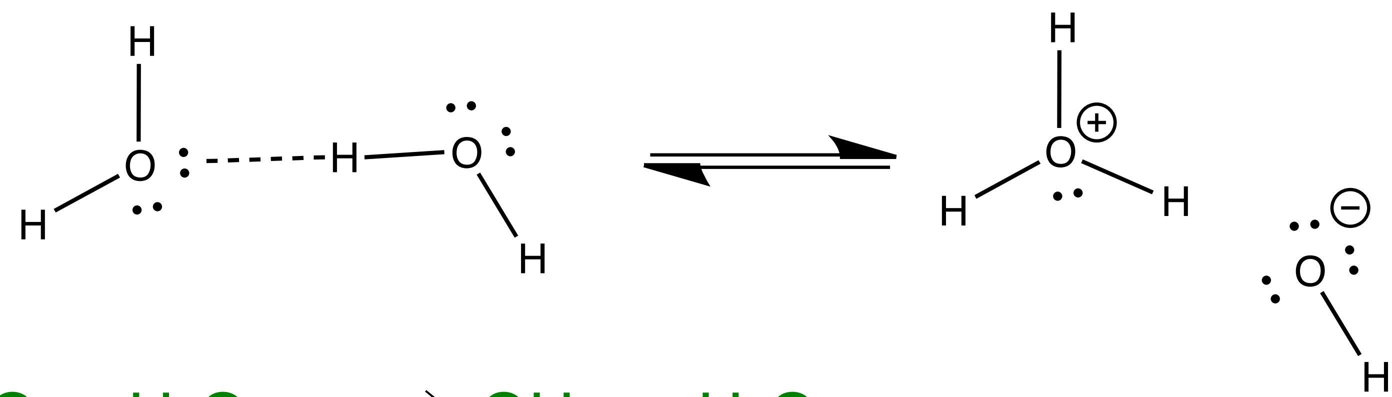
acidic   neutral   basic

$= -\log[H_3O^+]$

Use a log scale because we have very small numbers (10^{-7} 10^{-14} to 10^{-1}) pH 1 is very acidic.

Hydrogen ion concentration & pH

Autoionization of water:



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

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

$[H_2O] =$ constant (water concentration much higher than anything else)

$$K_W = [H_3O^+][OH^-] = 1x10^{-14}$$

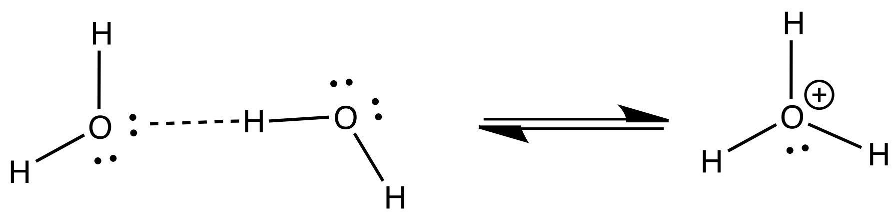
$$pK_W = 14$$

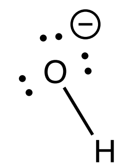
$$[H_3O^+] = [OH^-] = 10^{-7} M$$

$$pH + pOH = pK_W = 14$$

Hydrogen ion concentration & pH

Autoionization of water:





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

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

$[H_2O] =$ constant (water concentration much higher than anything else)

$$K_W = [H_3O^+][OH^-] = 1x10^{-14}$$

$$pK_W = 14$$

$$pH + pOH = pK_W = 14$$

What is the definition of a neutral solution? $[H_3O^+] = [OH^-] = 10^{-7}M$

$$pH = pOH = 7$$

Salts and water

We've already covered some of this stuff before:

but most students find it annoying and complex

so we will talk about it some more.

What happens when a salt dissolves in water?

What is a salt?

An ionic compound

Does not have H^+ as cation or OH^- as base.

Salts and water

What happens when a salt dissolves in water?

1. Dissociation (cation swims away from anion)
2. Solvation (both ions surrounded by water)
3. possibly hydrolysis.

Salts dissolve with almost complete dissociation
The ions are then “solvated”, surrounded by water. With water pointing its dipole moment at the ion to stabilize it.
All this happens to all salts.

Salts and water

What happens when a salt dissolves in water?

1. Dissociation (cation swims away from anion)
2. Solvation (both ions surrounded by water)
3. possibly hydrolysis.

What about 3 (hydrolysis)?

Happens when one of the ions is a weak acid or base?

$$KF \longrightarrow K^+ + F^- \longrightarrow K^+(H_2O)_6 + F^-(H_2O)_6$$

What can happen next?

Salts and water

$$KF \longrightarrow K^+ + F^- \longrightarrow K^+(H_2O)_6 + F^-(H_2O)_6$$

What can happen next? 2 possible reactions with water:

$$K^+ + H_2O \rightleftharpoons KOH + H^+$$

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

Which if either happens?

Happens when one of the ions is a weak acid or base?

$KF \longrightarrow K^+ + F^- \longrightarrow K^+(H_2O)_6 + F^-(H_2O)_6$

What can happen next? 2 possible reactions with water:

$K^+ + H_2O \rightleftharpoons KOH + H^+$

$F^- + H_2O \rightleftharpoons HF + OH^-$

This one happens. Why?

Because HF is a weak acid. Therefore equil. Is toward HF

This one happens why?

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

F^- +	H_2O	$\rightleftharpoons$	HF +	OH^-
Base(w)	acid(w)		acid(w)	base(s)

$F^- + H_2O \rightleftharpoons HF + OH^-$

Base(w) acid(w) acid(w) base(s)

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

Compare to ionization of weak acid:

$HF + H_2O \rightleftharpoons F^- + OH^-$

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

When you multiply these 2 together, something cool:

$$K_a K_b = \frac{[F^-][H_3O^+]}{[HF]} \frac{[HF][OH^-]}{[F^-]} = [H_3O^+][OH^-] = K_W$$

$$K_a K_b = K_W$$

The stronger the acid, the weaker the conjugate base. K_a big, K_b small.

Examples: $\rightleftharpoons$

1. What happens when sodium acetate dissolves in water?

2. What happens when ammonium nitrate dissolves in water?

Examples:

1. What happens when sodium acetate dissolves in water?

$$NaCH_3CO_2 + H_2O \rightleftharpoons Na^+ + CH_3CO_2^-$$

$$Na^+ + CH_3CO_2^- + H_2O \rightleftharpoons Na^+ + CH3CO_2H + OH^-$$

A weakly basic solution is the result.

2. What happens when ammonium nitrate dissolves in water?

$$NH_4^+ + NO_3^- + H_2O \rightleftharpoons NH_3 + NO_3^- + H_3O^+$$

The result is a weakly acidic solution.

Previous examples:

Recognition of salts:

Examples:

		KOH	base, strong
KClO	**salt**, base, weak	HNO_3	acid, strong
KCN	**salt**, base, weak	CH_3CO_2H	acid, weak
$NaHCO_3$	**salt**, base, weak	HF	acid, weak
$CaSO_3$	**salt**, base, weak	H_3PO_4	acid, weak
NH_4ClO_4	**salt**, acid, weak		
NH_4F	**salt**, acid, weak	NH_3	base, weak

Previous examples:

In general:

Acid	base	example	solution
Strong	strong	$NaCl$	neutral
Strong	weak	HCl	acidic
weak	strong	$NaCN$	basic
Weak	weak	NH_4CN	depends?

Salts of polyprotic acids

Examples:

$NaHSO_4$ HSO_4^- still acidic (strong acid)

$NaHCO_3$ HCO_3^{2-} hydrolyzes so basic (weak acid)

$$H_2CO_3 \longleftarrow HCO_3^- \longrightarrow CO_3^{2-}$$

K_a=4.5x10^{-7} 4.8x10^{-11}

Can act as an acid or base, amphoteric.

A competition for H^+, who wins, who loses?

Depends on the equilibrium constant.

Salts of polyprotic acids

$$H_2CO_3 \longleftarrow HCO_3^- \longrightarrow CO_3^{2-}$$

$K_a=4.5x10^{-7}$ $K_a= 4.8x10^{-11}$

Hydrolysis:

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ $K_h=K_w/K_a=10^{-7}$

Ionization:

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ $K_a = 4.8x10^{-11}$

$K_h>K_a$ so HCO_3^- prefers to hydrolyze to give basic solution.

Other amphoteric species

HSO_4^-

HPO_4^{2-}

$H_2PO_4^-$

$H_2PO_3^-$

In short, the single anion of a polyprotic acid.

It can go either way, get reprotonated or get deprotonated again.