Chemistry, The Central Science, 11th edition
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Chapter 16
Acids and Bases

Acids and Bases

Some Definitions

- Arrhenius

$HBr_{(aq)} \rightarrow H^+_{(aq)} + Br^-_{(aq)}$

  - An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.
  - A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

$Ca(OH)_{2(aq)} \rightarrow Ca^{2+}_{(aq)} + 2OH^{1-}_{(aq)}$

Acids and Bases

Some Definitions

- Brønsted-Lowry
  - An acid is a proton donor. (H^+)
  - A base is a proton acceptor.

$HNO_3(g) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

acid, base

$NH_3(g) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

base, acid

Acids and Bases

A Brønsted-Lowry acid…

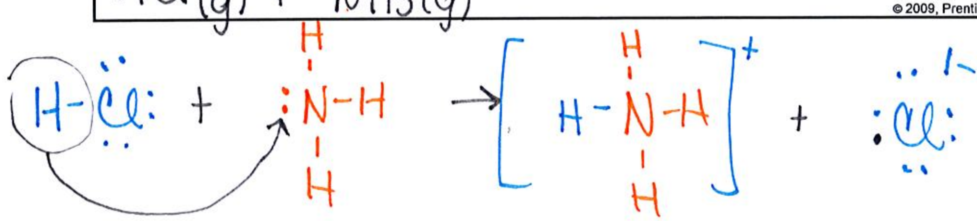
…must have a removable (acidic) proton.

A Brønsted-Lowry base…

…must have a pair of nonbonding electrons.

Acids and Bases

$HCl(g) + NH_3(g)$



If it can be either…

…it is amphiprotic.

acid $HCO_3^- + Cl^- \rightarrow HCl + CO_3^{-2}$

HCO_3^-

HSO_4^-

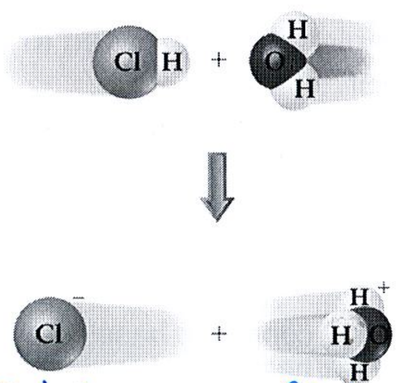
H_2O

base $HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$

→ can act as an acid or a base

Acids and Bases

What Happens When an Acid Dissolves in Water?



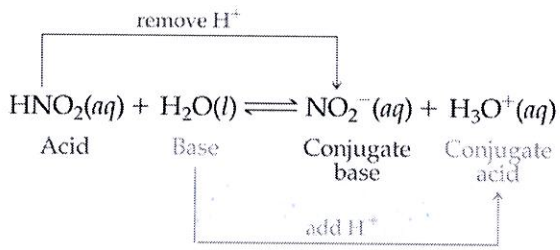
conj. base   conj. acid

- Water acts as a Brønsted-Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed. – H_3O^+

Acids and Bases

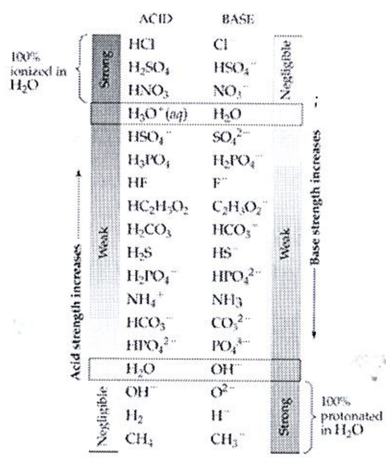
Conjugate Acids and Bases

- The term conjugate comes from the Latin word "conjugare," meaning "to join together."
- Reactions between acids and bases always yield their conjugate bases and acids.



Acids and Bases

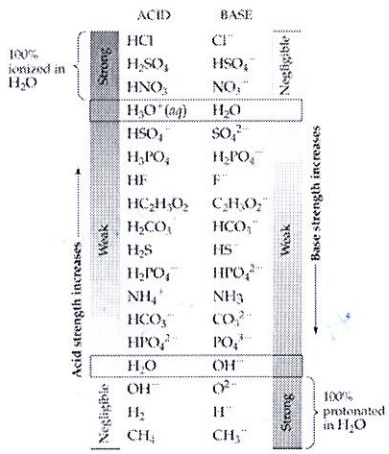
Acid and Base Strength



- Strong acids are completely dissociated in water.
  - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
  - Their conjugate bases are weak bases.

Acids and Bases

Acid and Base Strength



- Substances with negligible acidity do not dissociate in water.
  - Their conjugate bases are exceedingly strong.

Acids and Bases

Acid and Base Strength

- In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

very strong   very weak

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

A   B   CA   CB

- H_2O is a much stronger base than Cl^-, so the equilibrium lies so far to the right that K is not measured (K>>1).

$K = \frac{[products]}{[reactants]}$

$K >> 1$

Acids and Bases

Acid and Base Strength

- In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

$$CH_3CO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3CO_2^-\ (aq)$$

A B CA CB stronger

- Acetate is a stronger base than H_2O, so the equilibrium favors the left side ($K<1$).

$K_{eq} = \frac{[products]}{[reactants]}$ $K \ll 1$

Acids and Bases

Autoionization of Water

- As we have seen, water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.

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

A B CA CB

- This is referred to as autoionization.

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

Acids and Bases

Ion-Product Constant

- The equilibrium expression for this process is

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

- This special equilibrium constant is referred to as the ion-product constant for water, K_w.
- At 25°C, $K_w = 1.0 \times 10^{-14}$

Acids and Bases

pH

pH is defined as the negative base-10 logarithm of the concentration of hydronium ion.

$[H^+]$

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

Acids and Bases

pH

- In pure water,

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

- Since in pure water $[H_3O^+] = [OH^-]$,

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

$x \cdot x = 1.0 \times 10^{-14}$
$x^2 = 1.0 \times 10^{-14}$
$x = (1.0 \times 10^{-14})^{1/2}$
$x = 1.0 \times 10^{-7}\ M$

Acids and Bases

pH

perfectly neutral

- Therefore, in pure water,

$$pH = -\log(1.0 \times 10^{-7}) = 7.00$$

- An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7.
- A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.

Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	=7.00
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

Acids and Bases

Watch This!

Because

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

we know that

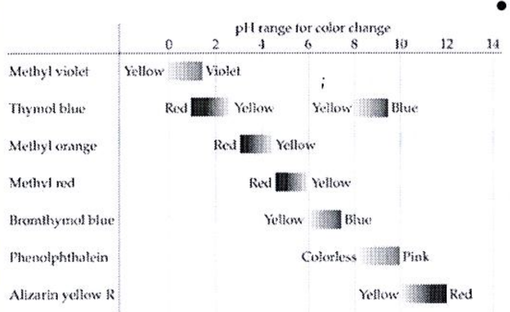
$$-\log\,[H_3O^+] + -\log\,[OH^-] = -\log K_w = 14.00$$

or, in other words,

$$pH + pOH = pK_w = 14.00$$

Acids and Bases

How Do We Measure pH?

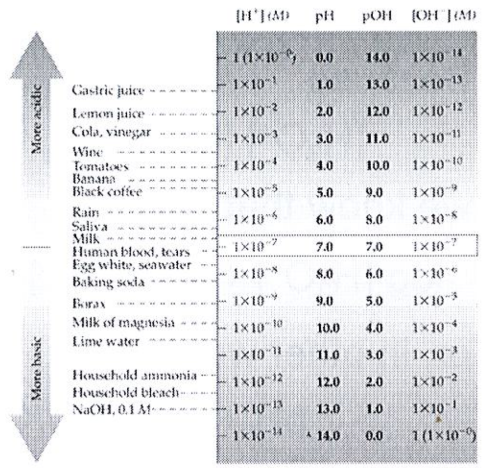


- For less accurate measurements, one can use
  - Litmus paper
    - “Red” paper turns blue above ~pH = 8
    - “Blue” paper turns red below ~pH = 5
  - Or an indicator.

Acids and Bases

pH

These are the pH values for several common substances.



Acids and Bases

Other "p" Scales

- The "p" in pH tells us to take the negative base-10 logarithm of the quantity (in this case, hydronium ions).
- Some similar examples are
  - pOH: $-\log [OH^-]$
  - pK_w: $-\log K_w$

Acids and Bases

Ex) Relative strengths of bases & predicting proton-transfer equilibrium

(1) For each of the following reactions, predict whether equilibrium lies predominantly to the left or the right.

(A) $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$

Left

(B) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

Right

pH Equations

1 $pH = -\log[H^+]$

2 $pOH = -\log[OH^-]$

3 $pH + pOH = pK_w = 14.00$

4 $[H^+][OH^-] = 1.0 \times 10^{-14}$

5 $[H^+] = 10^{-pH}$

6 $[OH^-] = 10^{-pOH}$

(2) In a sample of lemon juice, $[H^+]$ is 3.8×10^{-4} M. What is the pH?

$$pH = -\log(3.8 \times 10^{-4}) = 3.42$$

(3) A window cleaning solution has an $[OH^-]$ of 1.9×10^{-6} M. What is the pH?

$pOH = -\log(1.9 \times 10^{-6})$

$pOH = 5.72$

$pH + pOH = 14.00$

$pH + 5.72 = 14.00$

$pH = 8.28$

(4) A solution formed by dissolving an antacid tablet has a pH = 9.18. Calculate $[H^+]$

$$[H^+] = 10^{-9.18} = 6.61 \times 10^{-10} M$$

(5) A sample of fresh apple juice has a pH of 3.76. Calculate $[OH^-]$

$pH + pOH = 14.00$

$3.76 + pOH = 14.00$

$pOH = 10.24$

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

$= 10^{-10.24} = 5.75 \times 10^{-11} M$

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

$= 10^{-3.76} = 1.74 \times 10^{-4} M$

$[1.74 \times 10^{-4}][OH^-] = 1.00 \times 10^{-14}$

$[OH^-] = 5.75 \times 10^{-11} M$

How Do We Measure pH?

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.

Acids and Bases

$HNO_3(aq) \longrightarrow H^+_{(aq)} + NO_3^-(aq)$

we don't normally draw the ⇌ for strong acids (bases) because the reaction lies so far to the right (100% ions)

Strong Acids

- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic (H^+) strong acids,

$$[H_3O^+] = [acid].$$

So, calculating the pH is straightforward, for all strong acids (except H_2SO_4).

Acids and Bases

Why? The acid is normally the only significant source of H^+ ions!

* unless the $[H^+]$ is $< 10^{-6}$ M, then we would have to consider the H^+ ions that come from the autoionization of H_2O

Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}). $Ca(OH)_2(aq) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$
- Again, these substances dissociate completely in aqueous solution.
- strongly basic solutions are also made when certain substances react w/ H_2O to form OH^-; a common one is a substance w/ O^{2-}

$Na_2O(aq) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

Acids and Bases

Strong Bases

- $LiOH$
- $NaOH$
- KOH
- $RbOH$
- $CsOH$

From group 1

- $Ca(OH)_2$
- $Sr(OH)_2$
- $Ba(OH)_2$

From lower part of group 2

Example time!

Weak Acids Dissociation Constants

- For a generalized acid dissociation,

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

the equilibrium expression would be

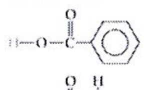
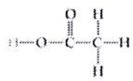
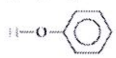
$$K_c = \frac{[H_3O^+][A^-]}{[HA]}$$

- This equilibrium constant is called the acid-dissociation constant, K_a.

Acids and Bases

Dissociation Constants

The greater the value of K_a, the stronger is the acid.

Acid	Structural Formula*	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)	H—F	F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5COO^-(aq)$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	H—O—Cl	ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

* The proton that ionizes is shown in blue.

The larger the value of Ka, the stronger the acid!

Acids and Bases

Calculating K_a from the pH

The pH of a 0.10 M solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

$HCOOH \rightleftharpoons H^+ + COOH^-$

We know that

$$K_a = \frac{[H_3O^+][COOH^-]}{[HCOOH]}$$

Acids and Bases

Calculating K_a from the pH

The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

To calculate K_a, we need the equilibrium concentrations of all three things.

We can find $[H_3O^+]$, which is the same as $[HCOO^-]$, from the pH.

Acids and Bases

Calculating K_a from the pH

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

$[H^+] = 10^{-2.38}$

$[H^+] = 4.17 \times 10^{-3}$

$=$

$[COOH^-]$

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

$$2.38 = -\log [H_3O^+]$$

$$-2.38 = \log [H_3O^+]$$

$$10^{-2.38} = 10^{\log [H_3O^+]} = [H_3O^+]$$

$$4.2 \times 10^{-3} = [H_3O^+] = [HCOO^-]$$

Acids and Bases

(6) what is the pH of a solution made by dissolving .010 mol of Na_2O in enough water to form 1.0 L of solution

$$\underset{.010\,M}{Na_2O\ (aq)} \rightarrow 2Na^+ + \underset{.020\,M}{2OH^-}$$

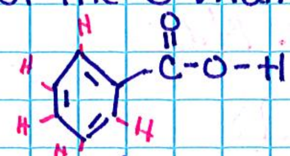
$\frac{.010\ mol}{1.0\ L}$

$pOH = -\log[OH^-] = -\log[.020] = 1.70$

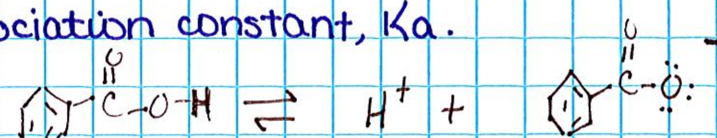
$pH + 1.70 = 14.00$

$pH = 12.30$

(7) Niacin, one of the B vitamins, has the following molecular structure:



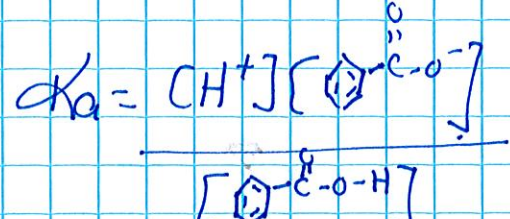
A .020 M solution of niacin has a pH of 3.26. what is the acid-dissociation constant, Ka.



I	.020 M	0 M	0 M
C	-.00055 M	+.00055 M	+.00055 M
E	.01945 M	.00055 M	.00055 M

$[H^+] = 10^{-3.26}$

$[H^+] \cong 5.5 \times 10^{-4}\ M$



$= \frac{[.00055][.00055]}{[.01945]}$

$= 1.56 \times 10^{-5}$