Acids & Bases

Chapter 14

Arrhenius

Acids – general formula is HX

- produce H^+ (or H_3O^+) in aqueous solution
- $HX + H_2O \leftrightarrow H_3O^+ + X^-$

Bases – general formula is MOH (M = metal)

- produce OH^- in aqueous solution
- $MOH_{(s)} \rightarrow M^+_{(aq)} + OH^-_{(aq)}$

Arrhenius Theory is limited because:

1. it's only good for aqueous solutions
2. it only dealt with one type of base – hydroxides

Brönsted – Lowry

Acid – proton donor (H^+ is a proton)

Base – proton acceptor

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightarrow H_3O + Cl^-$$

Ex.

In general:

$$\underset{\text{Acid}}{HA_{(aq)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightarrow \underset{\text{conjugate Acid}}{H_3O^+_{(aq)}} + \underset{\text{conjugate Base}}{A^-_{(aq)}}$$

Conjugate Acid – Base Pair

- two substances related by the transfer of a proton (H^+)
- they have the same formula except that the acid has <u>one more proton</u>
- <u>strong</u> acids have <u>weak</u> conjugate bases
- <u>weak</u> acids have <u>strong</u> conjugate bases

Many acid base reactions can be viewed as "competition" for a proton

$A^- \leftrightarrow H \leftrightarrow H_2O$

The stronger base ends up with the proton (has a greater affinity for it)

Structure of Acids

- any substance containing H^+ can act as an acid
- the strenth of the acid depends on
  1. the strength of the H-X bond
  2. the polarity of the H-X bond

1. The stronger the H-X bond, the <u>weaker</u> the acid.

	Bond Strength (Kj/mol)	Acid Type
HF	565	Weak
HCl	427	Strong
HBr	363	Strong
HI	295	Strong

2. The <u>more polar</u> the H-X bond, the <u>stronger</u> the acid
   - the <u>greater</u> the number of oxygen atoms present, the greater the attraction for the pair of electrons shared between O-H.
     - the <u>more O's</u> present in a member of an oxyacid family, the <u>stronger</u> the acid
   - for <u>different</u> central atoms, the <u>greater the charge</u> on the central atom, the <u>stronger</u> the acid

ex. Strongest → Weakest most O's, largest charge on Cl
$HClO_4$, $HClO_3$, $HClO_2$, $HClO$, least O's, smallest charge on Cl

ex. Strongest → Weakest $HClO_3\ (Cl^{+5})$, $H_2SO_3\ (S^{+4})$, $H_3BO_3\ (B^{+3})$

Acid Strength

- determined by the amount of dissociation of the acid in H_2O

$HA + H_2O = H_3O^+ + A^-$

K_a= acid dissociation constant

- the larger the value of K_a the stronger the acid

$HA = H^+ + A^-$ ($[H_2O]$ is so large that it is essentially constant and drops out.)

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Strong Acids

- are considered to be 100% dissociated
  (you know these 6: $HClO_4$, HNO_3, H_2SO_4 (for 1 of the $H^{+'}$s), HI, HBr, HCl)
- for strong acids the equilibrium lies far to the <u>right</u>

$HA \rightleftarrows H^+ + A^-$ (~100% diss.)

- in solution the given $[HA] = [H^+]$
- strong acids have very weak conjugate bases
- for a strong acids K_a=very large (no numeric value)

Weak Acids

- dissociate only a small amount in H_2O

- most of the molecules remain undissociated
- the equilibrium lies far to the left

$$HA \rightarrow \Large\leftarrow \normalsize H^+ + A^-$$

- weak acids have conjugate bases that are stronger bases than H_2O
- for a weak acid, K_a=a small numeric value

Water

- is an amphoteric substance
- it can act as an acid or a base
- water undergoes "autoionization"

$$H_2O + H_2O = H_3O^+ + OH^-$$

or

$$H_2O = H^+ + OH^-$$

- the dissociation constant for H_2O is K_w

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

or

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

at 25°C

$$[H^+]=[OH^-]=1.0\text{x}10^{-7}M$$

$$\therefore K_w=(1\text{x}10^{-7})(1\text{x}10^{-7})=\boxed{1.0\text{x}10^{-14}}$$

- in any aqueous solution at 25°C

$$[H^+]\text{x}[OH^-]=1\text{x}10^{-14}$$

If a Solution is:

- Neutral, then $[H^+]=[OH^-]$
- Acidic, then $[H^+]>[OH^-]$
- Basic, then $[H^+]<[OH^-]$
- but in all cases, at 25°C,

$$[H^+][OH^-]=1\text{x}10^{-14}$$

- since $K_w=[H^+][OH^-]$ then: $[H^+]=\frac{K_w}{[OH^-]}$ or $[OH^-]=\frac{K_w}{[H^+]}$

14.3 (p654)

Find the $[H^+]$ or $[OH^-]$ and the character of the solution for:

a) $1.0\text{x}10^{-5}M\ OH^-$

b) $1.0\text{x}10^{-7}M\ OH^-$

c) 10.0 M H^+

The “p” function

p means “-log of”

ex. pX = -logX

---

pH Scale

- a compact way to represent a solutions acidity **$pH=-log[H^+]$**

ex. $[H^+]=1.0x10^{-9}M$ $pH=-log\ 1.0x10^{-9}=\boxed{9.0}$

***the # of decimal places in the pH should be the same as the # of sig. figs. in the $[H^+]$

(on your sci. calculator: $(1.0x10^{-9})$(log10g)(+/-) will give the pH=9)

- each change of 1 on the pH scale indicates a power of <u>10</u> change in the $[H^+]$

  $[H^+]=1.0x10^{-6}$ pH=6

  $[H^+]=1.0x10^{-7}$ pH=7

- the function “p” can be used on other numeric values

ex. $pOH = -log[OH^-]$

$pK = -logK$

This is a derivation of a formula. You <u>do not</u> need to be able to reproduce it. You only need to be able to work with the final formula.

- for any aqueous solution: $K_w=[H^+][OH^-]$
- taking logs of all values: $logK_w=log[H^+]+log[OH^-]$
- negating all terms: $-logK_w=-log[H^+]-log[OH^-]$
- but, -log=p, ∴ $pK_w=pH+pOH$
- and since at 25°C $pK_w=-log1.0x10^{-14}=14.00$

$$\boxed{pH+pOH=14.00 \quad @25^oC}$$

<u>14.6</u> (p657) Human blood, pH=7.41 @ 25°C

Calculate pOH, $[H^+]$ & $[OH^-]$

Calculating the pH of Strong Acid Solutions

- strong acids are considered to be <u>100%</u> dissociated
- therefore $[HA]=[H^+]$

ex. What is the pH of a 0.10M HNO_3 solution?

$[HNO_3]=[H^+]=0.10M$

$pH=-\log[H^+]=-\log 0.10= 1.00$

Calculating the pH of Weak Acid Solutions

- you must calculate the <u>equilibrium</u> $[H^+]$
- you must know the value of K_a for the acid
- you must use the initial [HA] to determine the equilibrium concentrations

ex. What is the pH of a solution that is known to be 1.00M HF?

for HF, $K_a=7.2x10^{-4}$ (small K_a so very little shift right)

<u>14.8</u> (p662) is another example of this type of problem (0.100M HOCl, $K_a=3.5x10^{-8}$)

Percent Dissociation

- Calculating the amount of a weak acid that does dissociate

$$\boxed{\%diss = \frac{AmountDissociated}{InitialConcentration} x100\%}$$

<u>14.10</u> (p666) % diss. of a)1.0M $HC_2H_3O_2$ \ $K_a=1.8x10^{-5}$
b) 0.100M $HC_2H_3O_2$ /

Up to now, we've only seen <u>mono</u>protic acids.

Polyprotic Acids

- contains more than one H^+
- dissociate in a step wise fashion

ex. Sulfuric Acid:

$H_2SO_4=H^+ + HSO_4^-$ K_a=very large
$HSO_4^-=H^+ + SO_4^{-2}$ $K_a=1.2x10^{-2}$ (fairly strong acid for 2nd dissociation)

ex. Phosphoric Acid

$H_3PO_4=H^+ + H_2PO_4^-$ $K_a=7.5x10^{-3}$
$H_2PO_4^-=H^+ + HPO_4^{-2}$ $K_a=6.2x10^{-8}$
$HPO_4^{-2}= H^+ + HPO_4^{-3}$ $K_a=4.8x10^{-13}$

Bases

- Arrhenius: $MOH \rightarrow M^+_{(aq)} + OH^-_{(aq)}$
- Brönsted-Lowry: a proton acceptor

Strong Bases

- alkali metal hydroxides (NaOH + KOH most common)
- dissociate in H_2O 100%
  ($Ba(OH)_2$+$Ca(OH)_2$ are considered fairly soluble)

Calculating the pH of a Strong Basic Solution

- for a strong base, $[MOH]=[OH^-]$

14.12 (p671) 5.0×10^{-2}M NaOH, pH=?

Nonhydroxide Bases

- in an aqueous solution they take a H^+ from a H_2O molecule
- let B=a base

$$\boxed{B_{(aq)}+H_2O = HB^+_{(aq)}+OH^-_{(aq)}}$$

- solution is basic because OH^- ions are produced in a solution
- B is usually the anion of a weak acid
- other notable bases are:
  - i. O^{-2} (strongest base)
    $O^{-2} + H_2O \rightarrow 2OH^-$
  - ii. NH_3 (ammonia)
    $NH_3 + H_2O = NH_4^- + OH^-$

K_b=the equilibrium constant for the reaction of a base with H_2O to form its conjugate acid & OH^-

$B+H_2O=HB^++OH^-$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

(H_2O is so large it is constant)

- o if K_b is small, the base is weak

Calculating the pH of a Weak Base Solution

14.13 (p674) 15.0M NH_3, $K_b=1.8\times10^{-5}$, pH=?

Here's the derivation of the relationship between K_a & K_b:

Acid	Base
$HB = H^+ + B^-$	$B^- + H_2O = HB + OH^-$
$K_a = \frac{[H^+][B^-]}{[HB]}$	$K_b = \frac{[HB][OH^-]}{[B^-]}$

so

$$k_a \times k_b = \left(\frac{[H^+][B^-]}{[HB]}\right)\left(\frac{[HB][OH^-]}{[B^-]}\right)$$

Salts

- ionic compounds that <u>do not</u> contain H^+ or OH^-
- if soluble in H_2O, they dissociate 100% to form separate ions
- the ions from the salt can produce a solution that is
    a. Neutral
    b. acidic or
    c. basic

Neutral Solutions

- salts that contain the <u>anion</u> of a <u>strong acid</u> and the <u>cation</u> of a <u>strong base</u>.
- neither ion reacts with H_2O so the solution remains neutral

ex. NaCl (HCl and NaOH)
KNO_3 (HNO_3 and KOH)

Acidic Solutions

A. contain the anion of a strong acid and NH_4^+ (cation of a weak base that can lose a proton

the NH_4^+ loses a proton

$NH_4^+ \leftrightarrow NH_3 + H^+$ (acid)

ex. 14.19 0.1 M NH_4Cl, for NH_3 $K_b = 1.8x10^{-5}$

Calculate the pH

B. contain the anion of a strong acid and a metal ion with a charge of +3 or greater

- the ion becomes hydrated in solution

ex. $Al(H_2O)_6^{+3}$

- the positive charge on the metal ion attracts the electrons in the OH bond
- this weakens the bond and allows H^+ to be released

$Al(H_2O)_6^{+3} \leftrightarrow Al(H_2O)_5OH^{+2} + H^+$

Basic Solutions

A. contain the anion of a weak acid and the cation of a strong base

ex. $NaC_2H_3O_2$

Na^+ does not react with H_2O but

$C_2H_3O_2^- + H_2O == HC_2H_3O_2 + OH^-$ (base)

$$k_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

if you need to find K_b, $K_b = K_w/K_a$

ex. 14.18 0.30 M NaF, for HF, $K_a = 7.2x10^{-4}$
pH =

Salts that contain the <u>anion</u> of a <u>weak acid</u> and the <u>cation</u> of a <u>weak base</u>
if $K_a > K_b$ solution is Acidic
$K_a < K_b$ solution is Basic
$K_a = K_b$ solution is Neutral

ex. 14.21
A. $NH_4C_2H_3O_2$
B. NH_4CN
C. $Al_2(SO_4)_3$

Acid – Base Properties of Oxides

<u>Oxides of Nonmetals</u>

- When dissolved in H_2O, produce acid solutions
    - ex. $SO_2 + H_2O \rightarrow H_2SO_3$ (acid rain)

    - $Cl_2O + H_2O \rightarrow 2\ HOCl$
- these are referred to as "Acidic Anhydrides" (acids without water)

Oxides of Metals

- when dissolved in H_2O, produce basic solutions
    - ex. $Na_2O + H_2O \rightarrow 2NaOH$
    - $CaO + H_2O \rightarrow Ca(OH)_2$
      (remember: $O^{2-} + H_2O \rightarrow 2OH^-$
    - these are referred to as "Basic Anhydrides" (bases without water)

One more (but little used) theory on Acids & Bases

Lewis Acid – Base Model

- remember Lewis (electron dot) diagrams.
- Acid = electron pair acceptor
- Base = electron pair donor

ex. $H^+ + :NH_3 \rightarrow NH_4^+$

$BF_3 + :NH_3 \rightarrow F_3BNH_3$

- This theory is too general to be of much use when studying acids and bases.