

Acids & Bases

Chapter 14

Arrhenius

Acids – general formula is HX

- produce H^+ (or H_3O^+) in aqueous solution
- $\text{HX} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{X}^-$

Bases – general formula is MOH (M = metal)

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

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

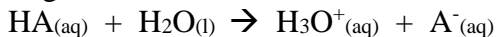
Acid – proton donor (H^+ is a proton)

Base – proton acceptor



Acid Base

In general:



Acid Base conjugate conjugate
Acid Base

Conjugate Acid – Base Pair

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

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



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 strength 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 weaker the acid.

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

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

ex. Strongest → Weakest most O's, largest charge on Cl
 HClO₄, HClO₃, HClO₂, HClO, least O's, smallest charge on Cl

ex. Strongest → Weakest HClO₃ (Cl⁺⁵), H₂SO₃ (S⁺⁴), H₃BO₃ (B⁺³)

Acid Strength

- determined by the amount of dissociation of the acid in H₂O

$$HA + H_2O = H_3O^+ + A^-$$
 - K_a= acid dissociation constant
 - o the larger the value of K_a the stronger the acid

$$HA = H^+ + A^- \quad ([H_2O] \text{ is so large that it is essentially constant and drops out.})$$
- $$K_a = \frac{[H^+][A^-]}{[HA]}$$

Strong Acids

- are considered to be 100% dissociated
 (you know these 6: HClO₄, HNO₃, H₂SO₄ (for 1 of the H⁺'s), HI, HBr, HCl)
- for strong acids the equilibrium lies far to the right



- 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 H₂O

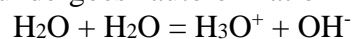
- most of the molecules remain undissociated
- the equilibrium lies far to the left



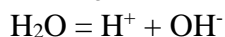
- weak acids have conjugate bases that are stronger bases than H_2O
- for a weak acid, K_a =a small numeric value

Water

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



or



- the dissociation constant for H_2O is K_w

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

or

$$K_w = [\text{H}^+][\text{OH}^-]$$

at 25°C

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

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

- in any aqueous solution at 25°C

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

If a Solution is:

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

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

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

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \quad \text{or} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

14.3 (p654)

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

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

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

c) 10.0 M H^+

The “p” function

p means “-log of”

ex. $\text{pX} = -\log \text{X}$

pH Scale

- a compact way to represent a solutions acidity $\text{pH} = -\log[\text{H}^+]$
ex. $[\text{H}^+] = 1.0 \times 10^{-9} \text{M}$ $\text{pH} = -\log 1.0 \times 10^{-9} = 9.0$
***the # of decimal places in the pH should be the same as the # of sig. figs. in the $[\text{H}^+]$
(on your sci. calculator: $(1.0 \times 10^{-9})(\log 10)(+/-)$ will give the $\text{pH}=9$)
- each change of 1 on the pH scale indicates a power of 10 change in the $[\text{H}^+]$
 $[\text{H}^+] = 1.0 \times 10^{-6}$ $\text{pH}=6$
 $[\text{H}^+] = 1.0 \times 10^{-7}$ $\text{pH}=7$
- the function “p” can be used on other numeric values
ex. $\text{pOH} = -\log[\text{OH}^-]$
 $\text{pK} = -\log \text{K}$

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

- for any aqueous solution: $K_w = [\text{H}^+][\text{OH}^-]$
- taking logs of all values: $\log K_w = \log[\text{H}^+] + \log[\text{OH}^-]$
- negating all terms: $-\log K_w = -\log[\text{H}^+] - \log[\text{OH}^-]$
- but, $-\log = \text{p}$, \therefore $\text{pK}_w = \text{pH} + \text{pOH}$
- and since at 25°C $\text{pK}_w = -\log 1.0 \times 10^{-14} = 14.00$

$$\text{pH} + \text{pOH} = 14.00 \quad @25^\circ\text{C}$$

14.6 (p657) Human blood, $\text{pH}=7.41$ @ 25°C
Calculate pOH , $[\text{H}^+]$ & $[\text{OH}^-]$

Calculating the pH of Strong Acid Solutions

- strong acids are considered to be 100% dissociated
 - therefore $[\text{HA}] = [\text{H}^+]$
- ex. What is the pH of a 0.10M HNO_3 solution?

$[\text{HNO}_3] = [\text{H}^+] = 0.10 \text{M}$

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

Calculating the pH of Weak Acid Solutions

- you must calculate the equilibrium $[\text{H}^+]$
- you must know the value of K_a for the acid
- you must use the initial $[\text{HA}]$ to determine the equilibrium concentrations

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

for HF, $K_a = 7.2 \times 10^{-4}$ (small K_a so very little shift right)

14.8 (p662) is another example of this type of problem (0.100M HOCl, $K_a = 3.5 \times 10^{-8}$)

Percent Dissociation

- Calculating the amount of a weak acid that does dissociate

$$\% \text{diss} = \frac{\text{Amount Dissociated}}{\text{Initial Concentration}} \times 100\%$$

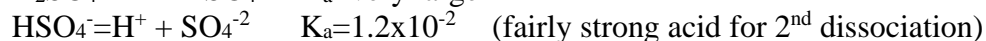
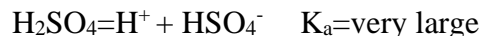
14.10 (p666) % diss. of a) 1.0M $\text{HC}_2\text{H}_3\text{O}_2$ \ $K_a = 1.8 \times 10^{-5}$
 b) 0.100M $\text{HC}_2\text{H}_3\text{O}_2$ /

Up to now, we've only seen monoprotic acids.

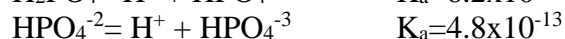
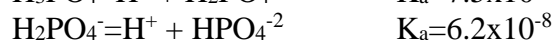
Polyprotic Acids

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

ex. Sulfuric Acid:



ex. Phosphoric Acid



Bases

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

Strong Bases

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

Calculating the pH of a Strong Basic Solution

- for a strong base, $[\text{MOH}] = [\text{OH}^-]$

14.12 (p671) $5.0 \times 10^{-2} \text{M NaOH}$, pH=?

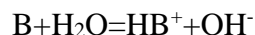
Nonhydroxide Bases

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



- solution is basic because OH^- ions are produced in a solution
- B is usually the anion of a weak acid
- other notable bases are:
 - O^{2-} (strongest base)
 $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$
 - NH_3 (ammonia)
 $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$

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



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

(H_2O is so large it is constant)

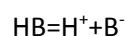
- if K_b is small, the base is weak

Calculating the pH of a Weak Base Solution

14.13 (p674) 15.0M NH_3 , $K_b = 1.8 \times 10^{-5}$, pH=?

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

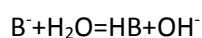
Acid



$$K_a = \frac{[H^+][B^-]}{[HB]}$$

[HB]

Base



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

[B⁻]

so

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

Salts

- ionic compounds that do not 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 anion of a strong acid and the cation of a strong base.
- neither ion reacts with H_2O so the solution remains neutral
- ex. $NaCl$ (HCl and $NaOH$)
- KNO_3 (HNO_3 and KOH)

Acidic Solutions

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

the NH_4^+ loses a proton
 $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ (acid)

ex. 14.19 0.1 M NH_4Cl , for NH_3 $K_b = 1.8 \times 10^{-5}$
 Calculate the pH

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

- the ion becomes hydrated in solution
- ex. $\text{Al}(\text{H}_2\text{O})_6^{+3}$
- the positive charge on the metal ion attracts the electrons in the OH bond
- this weakens the bond and allows H^+ to be released



Basic Solutions

A. contain the anion of a weak acid and the cation of a strong base
 ex. $\text{NaC}_2\text{H}_3\text{O}_2$

Na^+ does not react with H_2O but
 $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$ (base)

$$k_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]}$$

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

ex. 14.18 0.30 M NaF, for HF, $K_a = 7.2 \times 10^{-4}$
pH =

Salts that contain the anion of a weak acid and the cation of a weak base

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. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$

B. NH_4CN

C. $\text{Al}_2(\text{SO}_4)_3$

Acid – Base Properties of Oxides

Oxides of Nonmetals

- When dissolved in H_2O , produce acid solutions
 - ex. $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ (acid rain)

- $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{HOCl}$
- these are referred to as “Acidic Anhydrides” (acids without water)

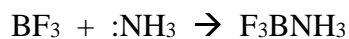
Oxides of Metals

- when dissolved in H_2O , produce basic solutions
 - ex. $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
 - $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
(remember: $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$)
 - 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. $\text{H}^+ + \text{:NH}_3 \rightarrow \text{NH}_4^+$



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