WEAK ACIDS AND BASES

[MH5; Chapter 13]

- Recall that a **strong** acid or base is one which **completely** ionizes in water.

$$HCl \rightarrow H^+ + Cl^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

- The above equations fit the Arrhenius definition of acids and bases; in water, acids produce H^+ and bases produce OH^-.
- The Brønstead-Lowry definition of acids and bases is better:
  * An acid is a proton (H^+) donor.
  * A base is a proton (H^+) acceptor.

- This means that in any acid-base reaction, a proton is transferred from the acid to the base.

- Consider the weak acid, HA: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
- The acid has transferred a proton to the water (which in this case is acting as a base).
- The H_3O^+ is what makes the solution acidic.
- The other species formed in this process is $\mathbf{A^-}$; we call this the **conjugate base** of the weak acid, HA.

- Now look at a weak base, B: $B + H_2O \rightleftharpoons BH^+ + OH^-$
- The base has taken a proton from the water (which in this case is behaving like an acid).
- The OH^- is what makes the solution basic.
- The other species formed in this process is $\mathbf{BH^+}$; this is the **conjugate acid** of the weak base B.

- Notice that water appears in both of these equations; it can either accept or donate a proton.
- Species such as this are termed **amphiprotic** or **amphoteric**.

$$OH^- \xleftarrow{-H^+} H_2O \xrightarrow{+H^+} H_3O^+$$

- So, what is the difference between a strong acid (or base) and a weak acid (or base) ?
- Strong acids and bases completely ionize in solution, whereas weak acids and bases do not.
- Because the ionization of a weak acid or base in water is incomplete, an equilibrium is established.
- It is, therefore, controlled by an equilibrium constant; K_a for acids and K_b for bases.
- For the weak acid, HA:

- For the weak base, B:

Notice that....

- $[H_2O]$ (constant at $\approx$ 55.6 M) does not appear in K_a or K_b.
- The larger the K_a the stronger the acid; the larger the K_b the stronger the base.

EXAMPLE:

CCl_3COOH; $K_a = 2.0 \times 10^{-1}$ is a stronger acid than...
CH_3COOH; $K_a = 1.8 \times 10^{-5}$

CH_3NH_2; $K_b = 6.4 \times 10^{-4}$ is a stronger base than...
NH_3; $K_b = 1.8 \times 10^{-5}$

- Hydrogen atoms on Carbon are not (generally) acidic in water.... for example, CH_3COOH is monoprotic (gives up one H^+)

- We may define pK_a analogous to pH and pK_w:

$pK_a = -\log K_a$ **$pK_b = -\log K_b$**

EXAMPLES:

pK_a for CCl_3COOH = 0.70 $[-\log (2.0 \times 10^{-1})]$
pK_a for CH_3COOH = 4.74 $[-\log (1.8 \times 10^{-5})]$

pK_b for CH_3NH_2 = 3.19 $[-\log (6.4 \times 10^{-4})]$
pK_b for NH_3 = 4.74 $[-\log (1.8 \times 10^{-5})]$

- Because of the minus sign, the smaller the value of K_a or K_b the larger the value of pK_a, or pK_b

OR

- The weaker the acid or base, the larger the pK_a or pK_b.....

Calculations Involving Weak Acids

- Suppose that we have a solution of acetic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$); let its initial concentration be represented by "**c**" $molL^{-1}$.
  At equilibrium, "**x**" mol L^{-1} have dissociated.....

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

- This is a quadratic equation in "**x**".

- The quadratic equation may be simplified by assuming that "**x**" is negligible compared to "**c**".
- CH_3COOH **is** a weak acid; so we may assume that the small amount dissociation makes little difference to the amount of undissociated acid left.
- Now let "c" = 0.10 $molL^{-1}$.....

- If **x** is negligible compared to 0.10 $molL^{-1}$:

  So...

- In this case, **x** is about 1.3% of 0.10, a negligible error within the accuracy of the original data we were given.
- If we were to solve the equation exactly, **x** = 1.333×10^{-3} M, so the approximate answer 1.342×10^{-3} M only differs from the exact answer by 0.009×10^{-3}, an "error" of less than 1%.

General Guideline:

- This **assumption**; a 'negligible' amount of the acid being ionized - is valid if **x** $\leq$ 5% of the initial concentration of acid.....
- This will generally be the case if the concentration of the acid, **c**, divided by the $\mathbf{K_a}$ value is > 100.

EXAMPLE: $[CH_3COOH] = 0.10$ M; $K_a = 1.8 \times 10^{-5}$

Test the assumption that $c - x \approx c$:

- The quantity [x /c] x 100 is called the degree of dissociation, expressed on a % basis; may also be called **percent dissociation** or **ionization**.

  Percent dissociation = $\frac{\text{Amount dissociated}}{\text{Original amount}} \times 100\%$

  =

- We can also use **x** to calculate pH; because in a weak acid equilibrium; **x** = $[H^+]$

  $[H^+] = 1.34 \times 10^{-3}$ M, therefore pH = 2.87

- The degree of dissociation **increases** as the solution is diluted, **although $[H^+]$ decreases.**

EXAMPLE: For solutions of HF in water:
K_a for HF = 6.7×10^{-4}

Initial [HF]	Equil. $[H^+]$	% Dissoc.	pH
1.0	2.6×10^{-2}	2.6	1.59
0.1	7.9×10^{-3}	7.9	2.10
0.01	2.3×10^{-3}	22	2.64
	decreasing	increasing	increasing

- What if we need to do the exact calculation?
- We have to solve the quadratic:

$$x^2 + K_a x - K_a C = 0$$

(from expansion of $K_a = x^2/(C - x)$

- What else can we calculate using K_a ??
- The K_a expression says:

- Depending on the information given, we could also calculate the initial concentration of the weak acid or the actual value of K_a.....

Strategy

- Always write the reaction for the weak acid given in the question.
- Write the equilibrium constant expression for the reaction.
- Identify what you know and what you are asked to find.
- Usually, it's a fairly straightforward matter of substituting for the appropriate variables in the Equilibrium Constant Expression.
- Sometimes there are a few intermediate calculations to perform....

EXAMPLE: Nitrous acid, HNO_2 has a K_a value of 6.0×10^{-4}.

a) Calculate the initial concentration of HNO_2 if a solution of this acid has a pH of 3.65.

b) Calculate the % ionization of HNO_2 in this solution.

Calculations Involving Weak Bases

- The most commonly used weak bases are Ammonia (NH_3) and its derivatives.
- In these compounds one (or more) N atom has a non bonding pair of electrons.

EXAMPLES:

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

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

- We may write K_b expressions for both of these……

- Problems using K_b are treated in the same manner as problems using K_a (weak acid).

EXAMPLE 1:

What is the % ionization and pH of a solution of a 0.0850 M solution of NH_3 ? $[K_b = 1.8 \times 10^{-5}]$

EXAMPLE 2:

Calculate the K_b for the weak base B, if a 0.00365 M solution of that base is 8.50 % ionized.

Conjugate Species

- Recall that a weak acid (HA), will produce its **conjugate base** (A^-) when it ionizes in water.

- The **conjugate base** of any acid is the species that is obtained from the acid by removal of one H^+ (or proton).

- A weak base (B), will produce its **conjugate acid** (BH^+) when it ionizes in water.

- Similarly, the **conjugate acid** of any base is the species that is obtained from the base by addition of a proton (or H^+).

- It is essential to realize that in any conjugate acid/base pair, the acid always has one more H than the base.
- You must be able to recognize conjugate bases and acids, based on the identity of the original weak acid or base !

EXAMPLES:

- Consider the weak acid HNO_2; its conjugate base is NO_2^-.
- Now look at the weak base NH_3 ; its conjugate acid is NH_4^+.
- HNO_2 / NO_2^- and NH_3 / NH_4^+ are **conjugate acid-conjugate base pairs** (the species in each pair differ by **one** H^+)

Reactions of Conjugate Species

- How do conjugate species behave when they are put in water ?
- Consider the generic weak acid, **HA**; its conjugate base is $\mathbf{A^-}$.
- This species will act as a base in what is often called **hydrolysis**.

- What is K_b for A^-, and how is it related to K_a for HA?

- Or...to get the same result, we could add the equations, and then (as we have seen earlier in these notes; p. 135) their K's are multiplied:

- The relationship $\mathbf{K_a \times K_b = K_w}$ is always true for a conjugate acid-base pair.
- The **weaker** the acid, the more **basic** is its conjugate base.

We can also use the log scale:

$$\mathbf{pK_a + pK_b = pK_w = 14.0}$$

EXAMPLE 1:

HF, a weak acid: $K_a = 7.24 \times 10^{-4}$; $pK_a = 3.14$

F^-, (conjugate base of HF)

$pK_b =$

$K_b =$

EXAMPLE 2:

HCN, a very weak acid: $K_a = 4.00 \times 10^{-10}$; $pK_a = 9.40$

CN^-, (conjugate base of HCN)

$pK_b =$

$K_b =$

- Now look at the generic weak base **B**, whose conjugate acid is **BH^+**.
- BH^+ will act like an acid; we call this one hydrolysis as well.

- We can determine K_a for this conjugate acid in the same manner as we determined K_b for a conjugate base, resulting in:

$$K_a = \frac{K_w}{K_b} \qquad \text{or} \qquad K_b \times K_a = K_w$$

- As was the case with the weak acids, the **weaker** the base, the more **acidic** is its conjugate acid.

EXAMPLE 1:
NH_3 is a weak base; $K_b = 1.8 \times 10^{-5}$; $pK_b = 4.74$
NH_4^+ (conjugate acid of NH_3); $pK_a =$
$K_a (NH_4^+) =$

EXAMPLE 2:
Aniline, $C_6H_5NH_2$, is a very weak base; $K_b = 4.0 \times 10^{-10}$; $pK_b = 9.40$
$C_6H_5NH_3^+$ (conjugate acid of $C_6H_5NH_2$) ; $pK_a =$
$K_a =$

Salts

- You may have noticed that the conjugate base of a weak acid, or the conjugate acid of a weak base is always an ion.
- So where does this ion come from?
- It is always produced when the "parent" weak acid or base ionizes, but these conjugate species can be also be found in ionic compounds.
- And ions are formed when an ionic solid is dissolved in water.....
- Remember those solubility rules ????
- This is where they come in handy; so you will know whether or not a solid will dissolve in water to produce ions!!

- First we consider salts that yield the conjugate base of a weak acid.
- Recall that the conjugate base will always behave like a base when in aqueous solution:

$$\mathbf{B + H_2O \rightleftharpoons BH^+ + OH^-}$$

EXAMPLE 1:

Consider the salt CH_3COONa. In water:

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

- The CH_3COO^- will now undergoes hydrolysis with water:

- The **ion** that is the **conjugate species** of a **weak acid** or **base** is the species that will undergo the **hydrolysis** with water.
- Remember that a conjugate species differs from its "parent" species by only one H^+ !!

EXAMPLE 2:

Calculate the pH of a 0.100 M solution of KF. [K_a for HF = 7.24×10^{-4}]

EXAMPLE 2:

A 0.0285M solution of the sodium salt, NaA of the weak monoprotic acid, HA, has a pH of 9.65. Calculate K_a for the acid, HA.

- Salts that produce the conjugate acids of weak bases will exhibit **acidic** behaviour in solution:

$$\mathbf{HA + H_2O \rightleftharpoons H_3O^+ + A^-}$$

EXAMPLE 1: What happens when NH_4Cl is placed in water?

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

The NH_4^+ is the conjugate acid of NH_3, so in water, hydrolysis occurs.

EXAMPLE 2: Calculate the pH of a solution of 0.175 M NH_4NO_3.

In water:

Then:

Equivalence Point of a Titration

- This is the point where the stoichiometric quantities of acid and base, defined by the equation, have been mixed together.
- It is **really** important to note that the solution is **NOT always** neutral (i.e. pH = 7) at the equivalence point !!
- This is why, earlier, we used the term **equivalence point** rather than neutralization point.
- The pH at the equivalence point is only truly neutral (pH = 7) for a titration of a **strong** acid with a **strong** base.

$$\mathbf{HC\ell} + \mathbf{NaOH} \rightarrow \mathbf{NaC\ell} + \mathbf{H_2O}$$

strong strong neutral

- So **why** is the solution of $NaC\ell$ neutral?
- Because neither $Na^+(aq)$ nor $C\ell^-$ is the conjugate of a weak species.
- If both ions which form the salt ($NaC\ell$ in this case) originally came from strong species, they may termed **spectator ions** and the solution will be neutral.

In contrast; look at the reaction of a weak acid with a strong base:

$$\mathbf{CH_3COOH} + \mathbf{NaOH} \rightarrow \mathbf{CH_3COO^-Na^+} + \mathbf{H_2O}$$

weak strong basic solution

- The salt formed in the reaction is $CH_3COO^-\ Na^+$.
- The CH_3COO^- is a base ; the conjugate base of the weak acid CH_3COOH.
- That means that this solution will be basic.

- Or, the reaction of a weak base with a strong acid:

$$\underset{\text{strong}}{HC\ell} + \underset{\text{weak}}{NH_3} \rightarrow \underset{\text{acidic solution}}{NH_4^+C\ell^-} + H_2O$$

- The salt formed in this reaction is $NH_4^+C\ell^-$.
- The NH_4^+ is an acid; the conjugate acid of the weak base NH_3.
- So this solution will be acidic.

- There is one other possible combination; that of a weak acid plus a weak base: this will be acidic or basic at equivalence depending upon the relative strengths of the acid and base involved..... Ignore!

- What is **really** happening at the equivalence point in titrations of a weak species with a strong species ?

1) $CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$
2) $HC\ell + NH_3 \rightarrow NH_4^+C\ell^- + H_2O$

- Because one of the species involved in the titration - CH_3COOH in (1) and NH_3 in (2) - is a **weak** species, the reactions are not quite complete (because the weak species never completely ionize.)
- They are, however, close enough to complete that we can assume that the salt is by far the major species at equilibrium.
- So... as a first approximation, we start our calculation by assuming complete reaction to the salt. [As shown by equations 1) & 2).]
- To correct this not-quite-true first approximation, we correct it by allowing a back reaction; this is hydrolysis of water by the salt.

3) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
4) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

- These hydrolysis reactions are actually the **ionic** equations corresponding to the reverse of (1) and (2) !!

- How do we put all this information together to solve an equivalence point problem ?

- The steps are:

  1) Write an equation for the acid base **reaction.** (Similar to equations 1) or 2) on the previous page.)

  2) Determine the number of moles of the acid and base……recall that at the equivalence point, these will be equal.

  3) Determine the number of moles of salt formed (equal to the number of moles of acid or base).

  4) Determine the total volume of the solution, and the Molarity of the salt solution.

  5) Now write an equation for the hydrolysis reaction by the salt. (Similar to equations 3) and 4) on the previous page.)

  6) Using K_w, calculate K_a or K_b for the salt.

  7) Now calculate the concentration of either the H_3O^+ or the OH^- formed as a result of hydrolysis.

  8) Finally, calculate the pH.

EXAMPLE 1:

Calculate the pH at the equivalence point of the titration of 25.00 mL of 0.165 M benzoic acid, C_6H_5COOH, with 0.185 M KOH.
[K_a for $C_6H_5COOH = 6.6 \times 10^{-5}$]

EXAMPLE 2:

Calculate the pH at the equivalence point of the titration of 0.175 M methylamine, CH_3NH_2, with 0.250 M HNO_3.

[K_b for $CH_3NH_2 = 6.4 \times 10^{-4}$]

Acid Base Indicators [MH5; 14.2]

- Indicators are used to detect the equivalence point of a titration.
- An indicator is a weak organic acid that has the particular property of being a noticeably different colour from its conjugate base.
- The indicator used must change colour at a pH that closely matches the pH expected at the equivalence point of the titration
- Over the small pH range where the acid changes over to the conjugate base, we see a change of colour.....

$$\mathbf{HIn \rightleftharpoons H^+ + In^-}$$

- At the **end-point**, the indicator is changing colour; this is when $[In^-] = [Hin]$

- At this point, K_a (aka K_{HIn}) = $[H^+]$ and pK_a (aka pK_{HIn}) = pH
- Note: This is the pK_a value of the **indicator**, not that of the acid being titrated !

- At 1 pH unit below this pK_a value (acidic) the indicator is 90% in the HIn form.
- At 1 pH unit above this pK_a value (basic) the indicator is 90% in the In^- form.
- The approximate range for colour change: 2 pH units.

Selection of Indicator

- The indicator must change colour near the equivalence point.
- For a strong acid/strong base titration: the pK_a of the indicator should be 5 -9 , although in practice the pH changes so rapidly at the end-point that **any** indicator is suitable.
- For a weak acid/strong base titration: the pK_a of the indicator must be in the basic region, for example: phenolphthalein, $pK_a \approx 9$
- For a strong acid/weak base titration: the pK_a of the indicator must be in the acidic region, for example: methyl orange, $pK_a \approx 3.4$

The Common Ion Effect

- Recall that the **common ion** effect refers to a system at equilibrium which has present an ion that is present as a result of that equilibrium, but is also present from some other source.
- Consider a solution of Acetic Acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

- When we place the acid in water, equilibrium is established very rapidly ($\approx 10^{-(8\text{-to-}10)}$ seconds).....

- What happens (non-quantitatively) to the percent dissociation of the acetic acid (CH_3COOH) if.....

- A strong acid is added to the same solution (so H^+ is the added "common ion")?
- Or, equivalently, the CH_3COOH ionizes into a solution of a strong acid, instead of into water? (For acid-base reactions in water, the order of addition is unimportant.)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

- How do we treat such problems **quantitatively?**

EXAMPLE 1:

A solution is 0.20 M in CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and 0.050 M in $HC\ell$. What the % ionization of the CH_3COOH ? What is the pH of this solution ?

- A similar situation arises if a weak base dissociates into a solution of a strong base (or, equivalently, a strong base is added to a solution of a weak base).

Polyprotic Acids [MH5;13.4, page 364]

- Polyprotic acids are those which have more than one "acidic" hydrogen.
- This means that they dissociate (or ionize) in stages, with K_a values for each step.

EXAMPLE: Carbonic acid is H_2CO_3

Step 1: $\mathbf{H_2CO_3} \rightleftharpoons \mathbf{H^+} + \mathbf{HCO_3^-}$ $\quad K_1 = 4.2 \times 10^{-7}$

Step 2: $\mathbf{HCO_3^-} \rightleftharpoons \mathbf{H^+} + \mathbf{CO_3^{2-}}$ $\quad K_2 = 4.8 \times 10^{-11}$

Overall: $\mathbf{H_2CO_3} \rightleftharpoons \mathbf{2\ H^+} + \mathbf{CO_3^{2-}}$ $\quad K_{overall} = K_1 \times K_2$

- These equilibria are typical of polyprotic acids; $K_1 >> K_2$.
- As a result: ≈ all the $[H^+]$ is due to the first acid ionization.....

- These dissociations also illustrate **simultaneous equilibria** in the acid dissociation of a polyprotic acid; both are happening at the same time.
- So both bicarbonate anion, HCO_3^-, **and** carbonate anion, CO_3^{2-}, are present in the equilibrium mixture in solution.

EXAMPLE:

Consider the acid dissociation of 0.25 M H_2CO_3.

What are the concentrations of all species in the equilibrium mixture, the % dissociation in each stage, and the pH?

[$K_1 = 4.2 \times 10^{-7}$, $K_2 = 4.8 \times 10^{-11}$]

First acid dissociation:

Second acid dissociation:

Because $K_2 << K_1$, the second acid dissociation does not affect either $[H^+]$ or $[HCO_3^-]$:

General Result: **for a diprotic acid H_2A in water; $[A^{2-}] = K_2$**

- Since K_2 is very small (4.8×10^{-11}), CO_3^{2-} is quite a strong base
- $K_b = 2.08 \times 10^{-4}$ (from $K_a \times K_b = K_w$).

EXAMPLE: What is the pH of 0.150 M Na_2CO_3 solution ?

In water:

Then the hydrolysis:

- Further reaction of HCO_3^- with H_2O is negligible;
  $K_b(HCO_3^-) = 2.38 \times 10^{-8} << K_b(CO_3^{2-}) = 2.08 \times 10^{-4}$

Note that HCO_3^- may act as either an acid or a base:

In water: $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ (acid)

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ (base)

OR: If acid or base is added to HCO_3^-.....

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-}$$