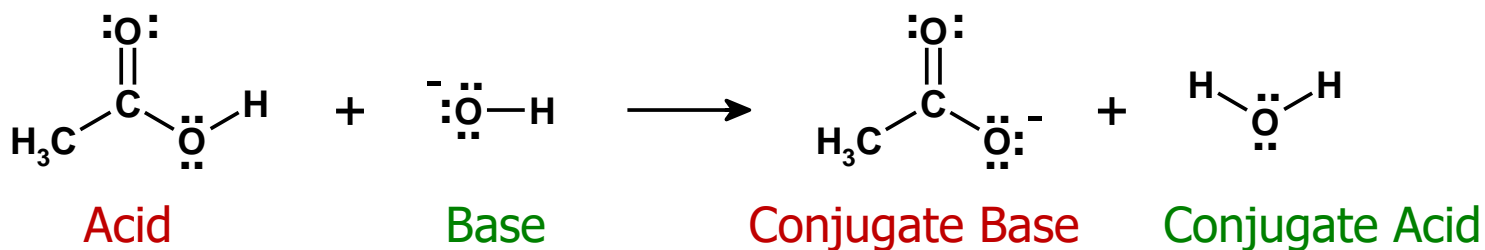# Organic Acids - Carboxylic Acids

Organic **acids** - **carboxylic acid** functional group.

Carboxylic **acids** are readily **deprotonated** by **bases** such as NaOH

e.g.

Acid   Base   Conjugate Base   Conjugate Acid

This reaction is **product favoured,** as the products are **more stable** than the reactants.

The **conjugate base** (acetate; $CH_3CO_2^-$) is much **more stable** than the **base** (hydroxide, OH^-); **therefore**,

       i) OH^- is a **stronger base** than $CH_3CO_2^-$.

       ii) CH_3CO_2H (pK_a = 4.7) a is **stronger acid** than H_2O (pK_a = 14).

Organic Acids

The **strength** of an **acid** is dependent on the **stability** of its **conjugate base**:

Conjugate base of HCl (a **strong acid**; pK_a= -7):

Cl⁻ (**stable** anion and thus a **very weak base**)

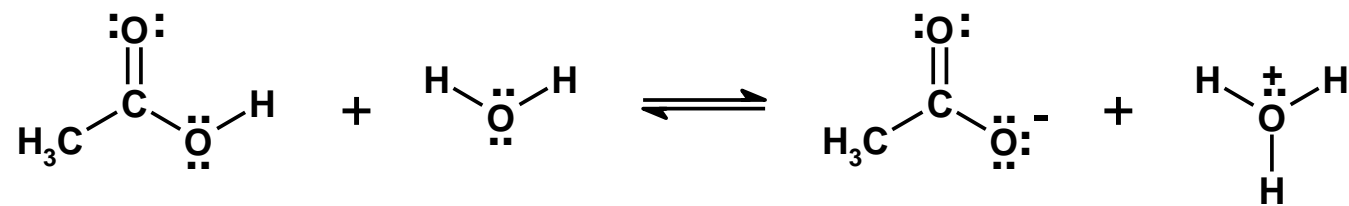**Conjugate base** of H_2O (a **weak acid**; pK_a= 14):

OH⁻ (**less stable** than Cl⁻ thus a relatively **strong base**)

The **strength** of an **acid** can also be said to be **inversely** related to the **strength** of its **conjugate base**.

Organic Acids (Carboxylic Acids)

Is the reaction below **product**- or **reactant**-favoured?

This reaction is equivalent to the **acid dissociation equation.**

as long as the solution is sufficiently dilute so that the $X_{H2O} \approx 1$,

its **equilibrium constant** is the K_a for CH_3CO_2H:

$$K_a = \frac{a_{H_3O^+} \cdot a_{CH_3CO_2^-}}{a_{CH_3CO_2H}}$$
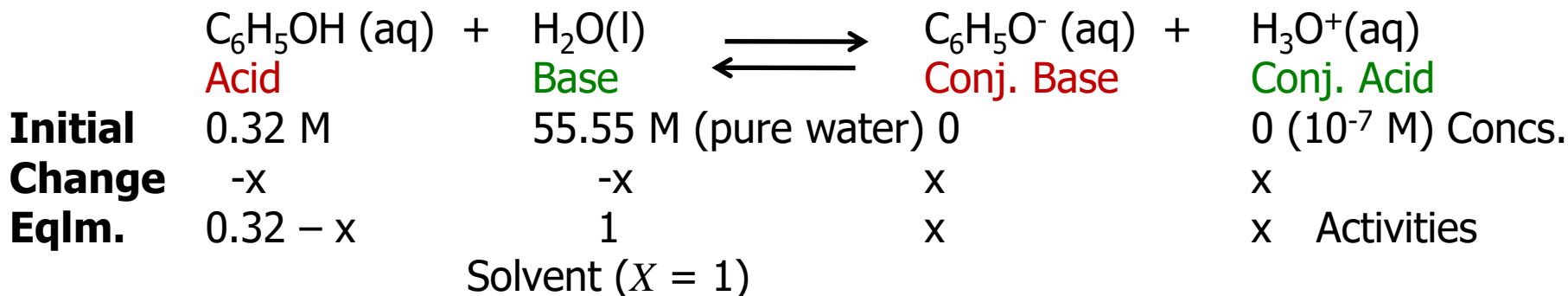
Recall that we can relate the K_a and pK_a for an acid via:

$$pK_a = -\log[K_a]$$

An **acid** is **stronger** if it has a **large** K_a and a **small** pK_a.

Calculating pH of an Acidic Solution

Consider a 0.32 M solution of phenol (pK_a=9.95) at 25.00 °C.

$$C_6H_5OH \text{ (aq)} + H_2O\text{(l)} \longrightleftharpoons C_6H_5O^- \text{ (aq)} + H_3O^+\text{(aq)}$$

	Acid	Base	Conj. Base	Conj. Acid
Initial	0.32 M	55.55 M (pure water)	0	0 (10^{-7} M) Concs.
Change	-x	-x	x	x
Eqlm.	0.32 – x	1	x	x Activities

Solvent ($X = 1$)

pK_a = 9.95 K_a = $10^{-9.95}$ = 1.122 * 10^{-10}

= a(Conj. Base) a(Conj. Acid)/a(Acid) a(Base)

= xx/(0.32 –x)   assume   x << 0.32

= x^2/0.32

x = ($1.122*10^{-10}$ * 0.32)$^{0.5}$ = $5.99*10^{-6}$ = [H_3O^+]

assumption valid?

pH = -log[H_3O^+] = 5.22

| X_o = $5.99*10^{-6}$ |
| X_1 = ($1.122*10^{-10}$*(0.32 – x_o))$^{0.5}$ = $5.99*10^{-6}$ |

Organic Acids

We can **increase** the strength of an **acid** by adding **electron-withdrawing** groups (usually very electronegative), further **stabilizing** its **conjugate base**.

To increase the **acidity** of acetic acid, **replace** one or more hydrogen atoms of the methyl group with **halogens**:
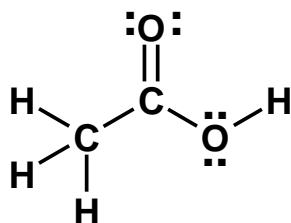
$$pK_a = 4.74$$

This **stabilization** through σ **bonds** is called an **inductive effect**.

Inductive effects are strongest when **close** to the **acidic hydrogen**.

NB: $CF_3CH_2CH_2CH_2CO_2H$ is not significantly more **acidic** than $CH_3CH_2CH_2CH_2CO_2H$

NB: Previously **inductive effects** were seen to affect the strength of the **oxoacids**.   (e.g. $HClO_2$ vs. $HClO_3$ vs. $HClO_4$)

Organic Acids

Carboxylic acids are among the **most acidic** organic molecules; however, a number of **other** functional groups contain **acidic hydrogen** atoms:

i) **Alcohols** are as **acidic** as water. Most have **pK_a's** of **~15-18.**

    NB: Inductive effects can **lower** these values to **~12**.

ii) **Phenols** are more **acidic** than alcohols. Most have **pK_a's** of **~8- 10.**

    NB: Their **pK_a's** can go as **low** as **1** with the right groups attached to the ring.

iii) **Thiols** (R-SH) are **more acidic** than alcohols. Most have **pK_a's** of **~10-12.**

    NB: Also subject to inductive effects.

iv) **Amines** are **not acidic** in water, but can be **deprotonated** by **strong bases** in **unreactive solvents** like alkanes or ethers. Their **pK_a's** are typically **~35-40**!

Calculating pH of an Acidic Solution

A **strong acid**, HA, (pK_a < 0) dissociates **fully** in water:

A **stronger acid** than H_3O^+ (pK_a = 0) generates H_3O^+ and **conj. base**, A^-.

This **effect** is known as **solvent leveling**:

No **acid stronger** than the **conjugate acid** of the **solvent** can exist in any solution of that solvent.

No **base stronger** than the **conjugate base** of the **solvent** can exist in any solution of that solvent.

Weak acids <u>aren't</u> subject to **solvent leveling**:

Consider the **percentage** of acid molecules that have **dissociated**.

In a **concentrated** solution of a **weak acid**, the **% dissociation** is **small**

Hence the **actual conc.** of **acid** is close to the **nominal conc.**

As a solution becomes more **dilute**, this **assumption** becomes **less** valid.

Calculating pH of an Acidic Solution

Consider a 4.2×10^{-5} M solution of CH_3CO_2H ($pK_a = 4.74$) at 25.00 °C.

$$CH_3CO_2H\ (aq)\ +\ H_2O(l) \rightleftharpoons CH_3CO_2^-\ (aq)\ +\ H_3O^+(aq)$$
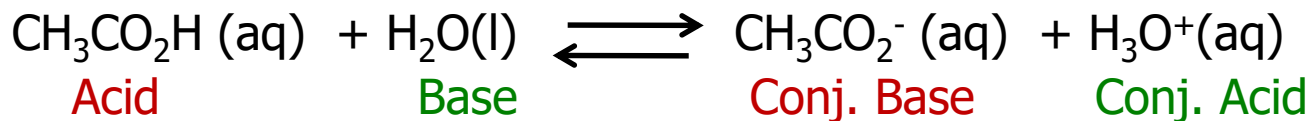
	Acid	Base	Conj. Base	Conj. Acid
Initial	4.2×10^{-5} M	55 M	0	0 (10^{-7} M) initial Conc.
Change	-x	-x	x	x
Eqlm.	$4.2 \times 10^{-5} - x$	1.0	x	x	activities at eqlm.

$pK_a = 4.74$ $K_a = 10^{-4.74}$

$$= 1.820 * 10^{-5}$$

$$= a(\text{Conj. Base})\ a(\text{Conj. Acid})/a(\text{Acid})\ a(\text{Base})$$

$$= x^2/(4.2 \times 10^{-5} - x) \quad => \quad 1.820*10^{-5}(4.2 \times 10^{-5} - x) = x^2$$

$$=> \quad x^2 + 1.820*10^{-5}\,x - 7.64*10^{-10} = 0$$

$$x = \{-1.820* 10^{-5} +/- [(1.820*10^{-5})^2 - 4(1)(- 7.64*10^{-10})]^{0.5}\}/2$$

$$= \{-1.820*10^{-5} +/- 5.821*10^{-5}\}/2$$

$$= 2.000 * 10^{-5} = [H_3O^+]$$

$$pH = -\log[H_3O^+] = -\log[2.00 * 10^{-5}] = 4.70$$

$X_o = 2.764*10^{-5}$ (+38%)
$X_1 = (1.82*10^{-5}(4.2*10^{-5} - 2.764*10^{-5})^{0.5}$
     $= 1.617*10^{-5}$ (-19%)
$X_2 = 2.168*10^{-5}$ (+8.4 %)
$X_3 = 1.923*10^{-5}$ (-3.9 %)
$X_4 = 2.036*10^{-5}$ (+1.8 %)
$X_5 = 1.985*10^{-5}$ (- 0.8 %)
$X_6 = 2.008*10^{-5}$ (+ 0.4 %) ......

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Distribution Curves

Working **backwards**, using the K_a equation, the **percent dissociation** of an acid at a given **pH** can be determined:

The **pH** tells us the **activity** of $H_3O^+_{(aq)}$, hence as long as the K_a value is **known**, the calculation proceeds as:

$$K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}} \qquad \text{so} \qquad \boxed{a_{HA} = \frac{a_{H_3O^+}}{K_a} a_{A^-}}$$

$$\% D = \frac{a_{A^-}}{a_{HA_0}} = \frac{a_{A^-}}{a_{A^-} + a_{HA}} = \frac{a_{A^-}}{a_{A^-} + a_{A^-}\dfrac{a_{H_3O^+}}{K_a}} = \frac{1}{1 + \dfrac{a_{H_3O^+}}{K_a}} = \boxed{\frac{K_a}{K_a + a_{H_3O^+}}}$$
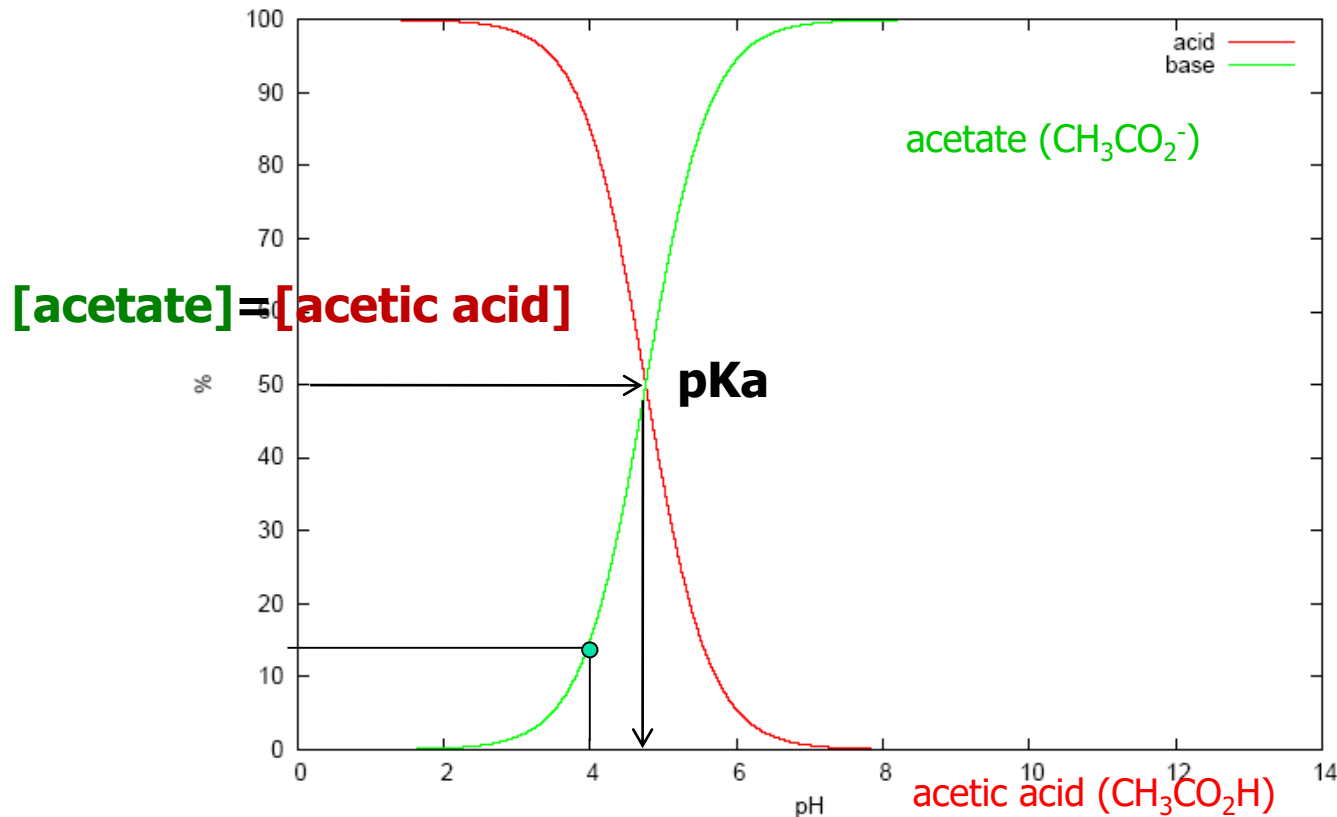
Calculate the percent dissociation of acetic acid ($pK_a=4.74$) at pH 4.00.

$$K_a = 10^{-4.74} = 1.820 * 10^{-5} \text{ M} \qquad a_{H3O+} = 10^{-4} \text{ M}$$

$$\% D = \frac{K_a}{K_a + a_{H_3O^+}} = \frac{1.82 * 10^{-5}}{1.82 * 10^{-5} + 1.00 * 10^{-4}} = \quad 0.154 \ = 15.4 \ \%$$

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Distribution Curves

If we repeat this calculation at a large number of different pH values, we generate what is known as a distribution curve:

NB: the two **curves cross** at the **pK$_a$** of the acid!

The pK$_a$ of an acid is the pH at which it is exactly 50% dissociated.

Distribution Curves

It is easy to see why an acid will be 50% dissociated at its pK_a. Consider the definition of pKa:

$$-\log\left(K_a\right) = -\log\left(\frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}}\right)$$

$$pK_a = -\log\left(a_{H_3O^+}\right) - \log\left(\frac{a_{A^-}}{a_{HA}}\right) = pH - \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

$$pH = pK_a + \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

Henderson-Hasslebalch equation.

note that if: $a_{A^-}/a_{HA} = 1$, then:

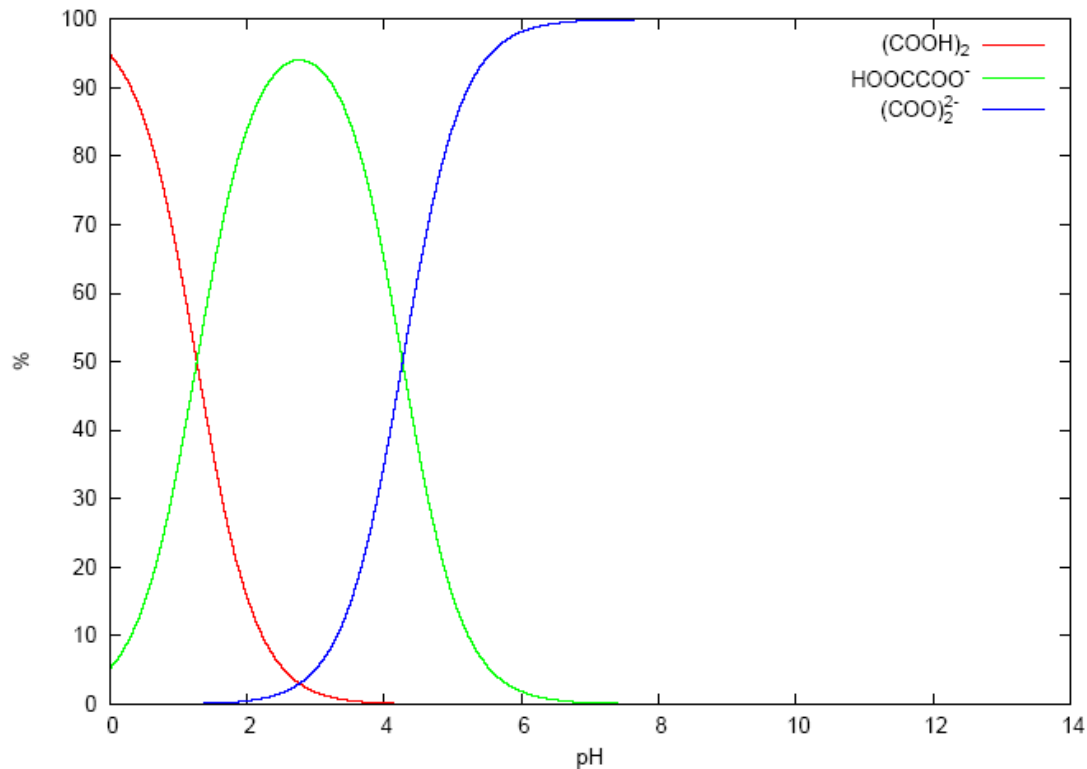$$\log\left(\frac{a_{A^-}}{a_{HA}}\right) = 0$$

hence :

$$pH = pK_a.$$

Distribution Curves for Polyprotic Acids

Consider an acid that has **multiple acidic protons** with pK_a values are different by several units.

The distribution curve will look like several monoprotic distribution curves superimposed
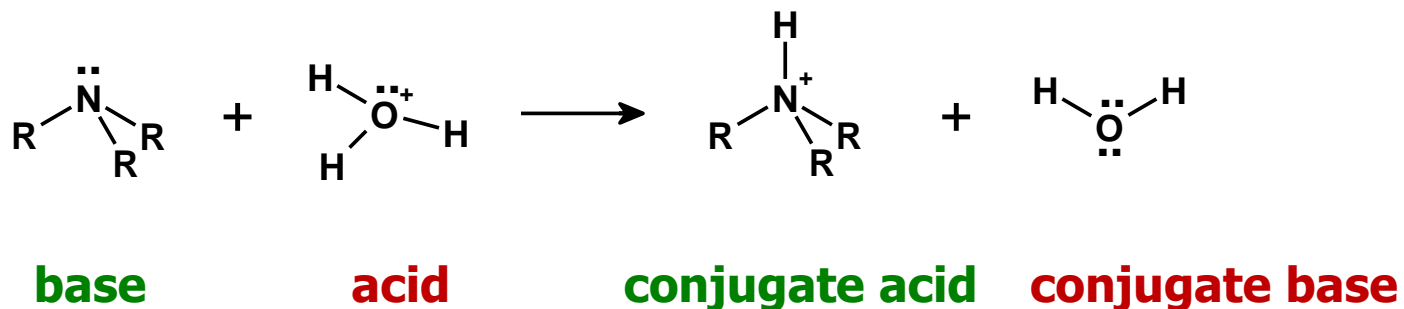
Ex) Oxalic Acid:

If the pK_a values are too close, the distribution curve will become more complex.

Organic Bases - Amines

Organic base: generally an **amine**.

Amines are readily **protonated** by acids:

e.g.

base   **acid**   **conjugate acid**   **conjugate base**

The basicity of amines is due to the **lone pair** on the nitrogen atom which makes **all** amines (R = H, alkyl or combination) **Lewis bases**.

Organic Bases

There are other functional group containing nitrogen.

Why is an amine considered a good base, but an amide is not?

The nitrogen atom of an amide is so weakly basic that the oxygen of the carbonyl group will be protonated over it!
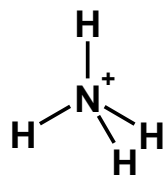
Quantifying Basicity

A base's **strength** is assessed by :

      1) K_b (or pKb)
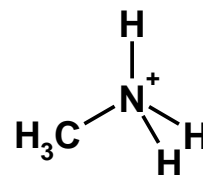
          or

      2) The K_a (or pK_a) of the **conjugate acid**.

        Since the strength of a base is **inversely** related to the strength of its **conjugate acid**,.
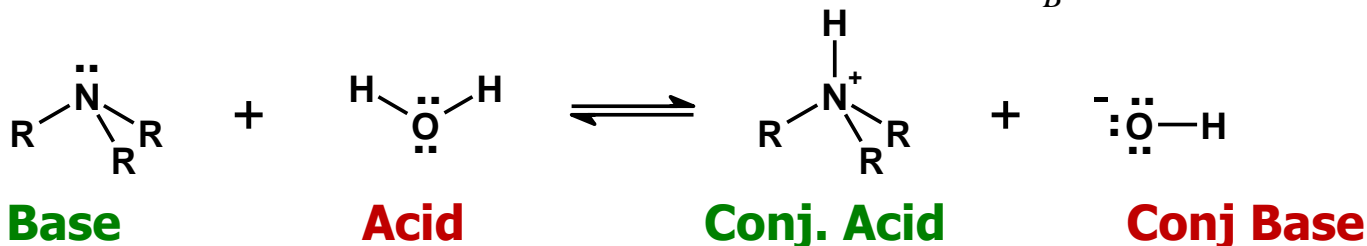
pKa = 9.3

pKa = 10.6

Smaller pK$_a$ = Stronger Conjugate Acid = Weaker Base

Quantifying Basicity: K_b

This is the equilibrium constant for reaction of the base with water:

$$K_b = \frac{a_{OH^-} \cdot a_{HB^+}}{a_B}$$

Base   **Acid**   **Conj. Acid**   **Conj Base**

K_b is inversely proportional to K_a for the conjugate acid:
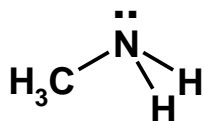
$$K_b = \frac{K_w}{K_a}$$

where $K_w = 10^{-14}$ under standard conditions.
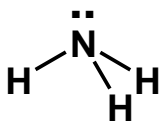
$$K_w = K_a \cdot K_b$$

$$-\log(K_a \cdot K_b) = -\log(K_w)$$

$$-\log(K_a) - \log(K_b) = -\log(K_w)$$

$$\rightarrow pK_a + pK_b = pK_w = 14$$

$pK_b = 3.4$ $pK_b = 4.7$

Larger K_b = Smaller pK_b = Stronger Base

Quantifying Basicity: K_b

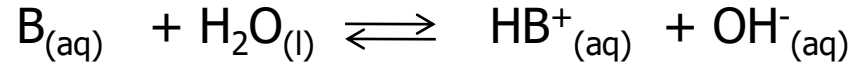**Ex)** Compute the K_b of aniline ($C_6H_5NH_2$) given that the pK_a of $C_6H_5NH_3^+$ is 4.7.

$$K_b = K_w/K_a$$

$$= 10^{-14}/10^{-4.7}$$

$$= 10^{-14}/2.00 * 10^{-5}$$

$$= 5.00 * 10^{-10}$$

$$pK_b = -\log(5.00 * 10^{-10}) = 9.30$$

Alternatively

$$pK_b = 14 - pK_a$$

$$= 14 - 4.7 = 9.30$$

Calculating pH of a Basic Solution

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

Using the K_b expression and nominal solution concentration to calculate a_{OH^-} then

$$K_b = \frac{a_{OH^-} \cdot a_{HB^+}}{a_B}$$

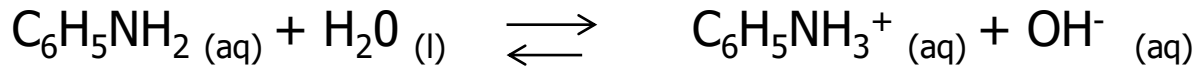Using the K_w expression calculate a_{H+} from a_{OH^-}

$$a_{OH^-} = \frac{K_w}{a_{H_3O^+}}$$

Recall: at 25 °C, $K_w = 10^{-14}$.

Finally use a_{H+} to calculate pH.

Calculating pH of a Basic Solution

Calculate the pH of a 0.71 M aqueous solution of aniline at 25 °C.

$$C_6H_5NH_{2\ (aq)} + H_2O_{(l)} \ \rightleftharpoons \ C_6H_5NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$$

Initial	0.71 M	55 M	0	0 (10^{-7} M)	Conc.
Change	-x	-x	x	x	
Eqlm	0.71-x	1	x	x	Activities

pKb = 10 => $K_b = 10^{-10}$

$$K_b = a(HB^+)a(OH^-)/a(B)\,a(H_2O)$$
$$= xx/(0.71 - x)$$

Assume x<< 0.71

$$10^{-10} = x^2/0.71$$

$$x = (10^{-10}*0.71)^{0.5} = 8.42*10^{-6}$$

$$a(OH^-) = 8.42*10^{-6}$$

$$a(H_3O^+) = Kw/\,a(OH^-) = 10^{-14}/\,8.42*10^{-6} = 1.188*10^{-9}$$

$$pH = -\log(1.188*10^{-9}) = 8.93$$

Alternatively : pOH = $-\log(8.42*10^{-6})$ = 5.07 pH = 14 − pOH = 8.93
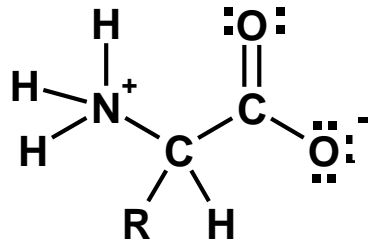
Amino Acids: Acid <u>and</u> Base

The structure of an amino acid is often shown as follows:
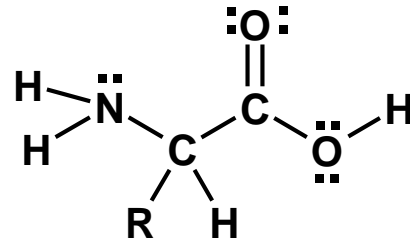
The name comes from having an **amine** group and a carboxylic **acid** group.

This is not how an amino acid actually exists under biological conditions (i.e. pH ~7).

Instead, it exists as the **zwitterion**:

Amino Acids: Acid <u>and</u> Base

Why is this?

The pK_a for the $-CO_2H$ proton is typically ~2 (slightly lower than the standard 3-5 range for carboxylic acids).

The pK_a for the conjugate acid of the amine group (i.e. for the $-NH_3^+$ proton) is typically ~9-10.

Exercise:

Use this data to sketch a distribution curve for the amino acid, labeling with the major species within each pH range.