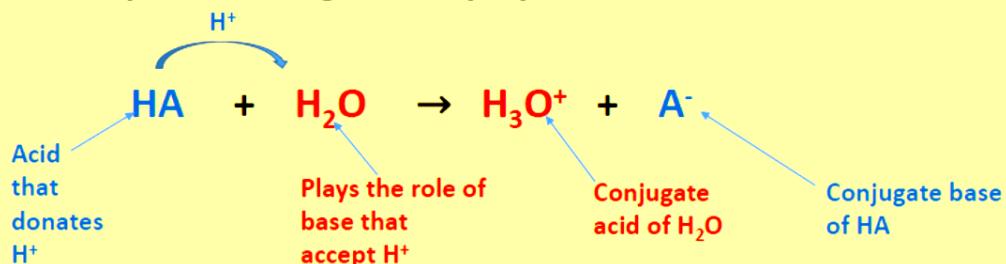


# Ch(6) : weak acid-weak base conjugate acid/base pairs

## I- Definition of acids and of bases according to Bronsted ( acid/base pairs)

An acid is a chemical species that is able to donate a proton ( $H^+$ ).

An acid is represented generally by  $HA$  :



Each acid has a conjugate base and each base has a conjugate acid.

Each acid with its conjugate base form an (acid/base) pair (couple) and it is simply represented by  $(A/B)$ .

The acid base pairs involved in the above reaction are :



A weak acid ( $HA$ ) is a chemical species that donates a proton  $H^+$  during an incomplete reaction (reversible) with water.



### Examples of weak acids:

$HCOOH$  (methanoic acid) :  $HCOOH + H_2O \leftrightarrow HCOO^- + H_3O^+$

Couples involved :  $(HCOOH/HCOO^-)$  and  $(H_3O^+/H_2O)$

$CH_3COOH$  (ethanoic acid) :  $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

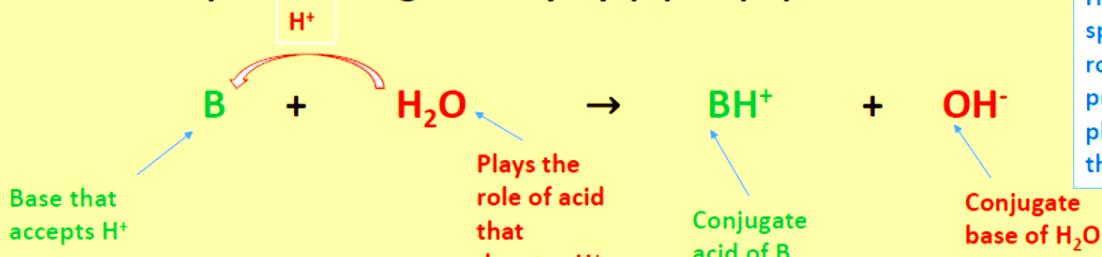
Couples involved :  $(CH_3COOH/CH_3COO^-)$  and  $(H_3O^+/H_2O)$

Generally :  $R-COOH$  (Carboxylic acids) :  $RCOOH + H_2O \leftrightarrow RCOO^- + H_3O^+$

Couples involved :  $(RCOOH/RCOO^-)$  and  $(H_3O^+/H_2O)$

A base is a chemical species that is able to accept a proton ( $H^+$ ).

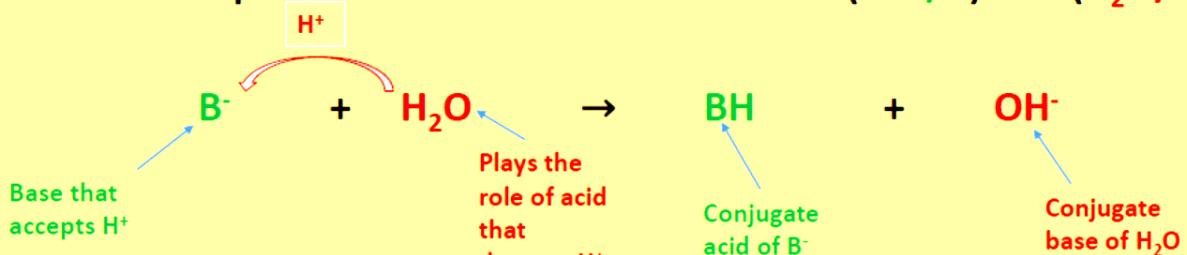
A base is represented generally by (B) or ( $B^-$ ).



Note

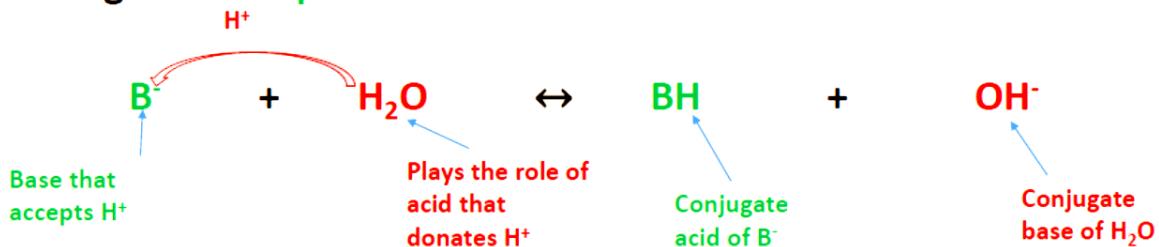
$H_2O$  is called amphoteric species since it plays the role of acid in the presence of base and plays the role of base in the presence of acid.

The couples involved in this reaction are : ( $BH^+/B$ ) and ( $H_2O/OH^-$ )



The couples involved in this reaction are : ( $BH/B^-$ ) and ( $H_2O/OH^-$ )

A weak base ( $B$  or  $B^-$ ) is a chemical species that is able to accept a proton  $H^+$  during an incomplete reaction with water



Examples of weak bases:

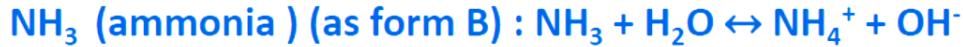


Couples involved : ( $HCOOH/HCOO^-$ ) and ( $H_2O/OH^-$ )

Generally :  $RCOO^-$  (carboxylate ions)(as form of  $B^-$ )



Couples ( $RCOOH/RCOO^-$ ) and ( $H_2O/OH^-$ )

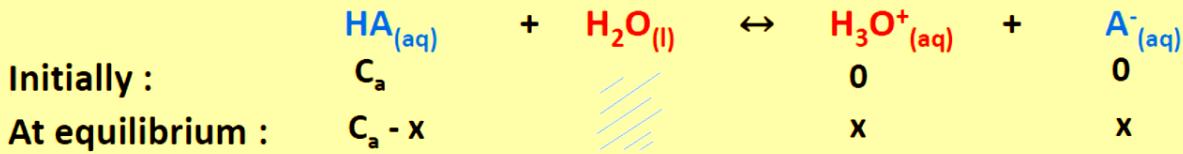


Couples involved : ( $NH_4^+/NH_3$ ) and ( $H_2O/OH^-$ )

## II- pH and degree of dissociation of weak acids

Consider a solution of weak acid HA of concentration  $C_a$ .

The equilibrium of the reaction of this acid with water is :



where we let  $x = [\text{H}_3\text{O}^+]$  formed at equilibrium

Acc. to. SR. at equilibrium:  $n(\text{HA})_{\text{reacted}} = n(\text{H}_3\text{O}^+)_{\text{formed}} = n(\text{A}^-)_{\text{formed}}$

By dividing by  $V_{\text{solution}}$ :  $[\text{HA}]_{\text{reacted}} = [\text{H}_3\text{O}^+]_{\text{formed}} = [\text{A}^-]_{\text{formed}} = x$

$$[\text{HA}]_{\text{remained}} = [\text{HA}]_0 - [\text{HA}]_{\text{reacted}} = C_a - x$$

The equilibrium constant of this reaction is designated by  $K_a$  (acidity constant) :

$$K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}]_{\text{rem}}} = \frac{x^2}{C_a - x} = \text{constant (given)}$$

By calculating x we obtain  $[\text{H}_3\text{O}^+] = x_{\text{calculated}}$

The pH of the solution is :  $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (x)$        $\text{pH} > -\log C_a$

$$x < C_a$$

If the pH of the solution is known, thus we can calculate x directly :

$$x = [\text{H}_3\text{O}^+]_{\text{formed}} = 10^{-\text{pH}}$$

The degree of dissociation  $\alpha$  of the weak acid HA is :

$$\alpha(HA) = \frac{n(\text{HA})_{\text{reacted}}}{n_0(\text{HA})} = \frac{[\text{HA}]_{\text{reacted}}}{[\text{HA}]_0} = \frac{x}{C_a} = \frac{10^{-\text{pH}}}{C_a}$$

Note

In the case of strong acids :

$$[\text{H}_3\text{O}^+]_{\text{formed}} = C_a \text{ (complete reaction)}$$

$$\text{pH} = -\log C_a$$

$$\alpha = 1 \text{ (100\%)}$$

The dilution 10 times increases the pH one unit.

$\alpha < 1$  (in the case of weak acids)

$$\alpha(HA) = \frac{x}{C_a}$$

Effect of dilution on the pH and on  $\alpha$  of weak acids

The dilution 10 times of solution of weak acid will rise its pH less than one unit.

### Note

Each weak acid (HA) is characterized by its specific equilibrium constant  $K_a$  that is different to the other weak acids.

### Application 1

A solution of ethanoic acid ( $\text{CH}_3\text{COOH}$ ) having a concentration  $C_a = 10^{-3} \text{ mol/L}$ .

1. Write the equation of the reaction of this acid with water.
2. Determine the pH of the solution knowing that the acidity constant of this acid is  $K_a = 1.7783 \times 10^{-5}$
3. Deduce the degree of dissociation  $\alpha$  of this acid.
4. The above solution is diluted 10 times. Calculate the new pH' and the new degree of dissociation  $\alpha'$ , compare and conclude.

### Answer



Where we let  $x = [\text{H}_3\text{O}^+]$  formed at equilibrium

$$K_a = \frac{[\text{CH}_3\text{COO}^-] \times [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_{\text{rem}}} = \frac{x^2}{10^{-3} - x} = 1.7783 \times 10^{-5}$$

$$x^2 + 1.7783 \times 10^{-5}x - 1.7783 \times 10^{-8} = 0$$

By solving the equation we obtain :

$$x_1 = 1.247 \times 10^{-4} \text{ mol/L} \quad \text{accepted}$$

$$x_2 = -1.425 \times 10^{-4} \text{ mol/L} \quad \text{rejected}$$

$$\text{pH} = -\log x = -\log (1.247 \times 10^{-4}) = 3.9$$

$$3. \alpha(\text{CH}_3\text{COOH}) = \frac{n(\text{CH}_3\text{COOH})_{\text{reacted}}}{n(\text{HA})_0} = \frac{x}{C_a}$$

$$= \frac{(1.247 \times 10^{-4})}{10^{-3}} = 0.124 (12.4\%)$$



Where we let  $x' = [\text{H}_3\text{O}^+]$  formed at the new equilibrium

$$K_a = \frac{[\text{CH}_3\text{COO}^-] \times [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COO}^-]_{\text{rem}}} = \frac{x'^2}{10^{-4} - x'} = 1.7783 \times 10^{-5}$$

$$x'^2 + 1.7783 \times 10^{-5}x' - 1.7783 \times 10^{-9} = 0$$

By solving the equation we obtain :

$x'_1 = 3.42 \times 10^{-5} \text{ mol/L}$  accepted

$x'_{2+} = -5.19 \times 10^{-5}$  mol/L rejected

$$\text{pH} = -\log x' = -\log (3.42 \times 10^{-5}) = 4.46$$

$$\alpha' (\text{CH}_3\text{COOH}) = \frac{n(\text{CH}_3\text{COOH})_{reacted}}{n(\text{CH}_3\text{COOH})_0} = \frac{x'}{C_a}$$

$$= \frac{(3.42 \times 10^{-5})}{10^{-4}} = 0.342 \text{ (34.2 %)}$$

$\text{pH}' = 4.46 > \text{pH} = 3.9$  ( pH increases  $<1$  unit upon dilution 10 times)

$\alpha' = 34.2\% > \alpha = 12.4\%$  (the dilution increases the dissociation of weak acid)

## Application 2

A solution of benzoic acid ( $C_6H_5COOH$ ) of concentration  $C_a = 10^{-4}$  mol/L has a pH = 4.11.

1. Write the equation of its reaction with water.
  2. Determine the acidity constant  $K_a$  of this acid.
  3. Calculate  $\alpha$

## Answer



Where we let  $x = [\text{H}_3\text{O}^+]_{\text{formed}} = 10^{-\text{pH}} = 10^{-4.11} \text{ mol/L}$

$$K_a = [C_6H_5COO^-][H_3O^+]/[C_6H_5COOH]_{\text{rem}} = x^2/(10^{-4}-x)$$

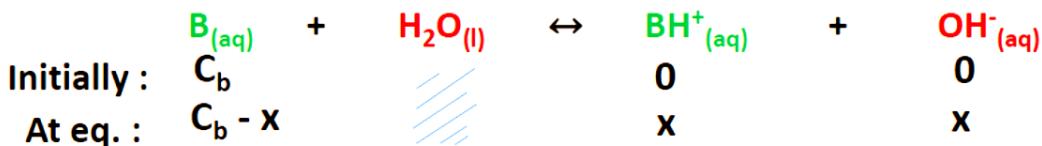
$$= (10^{-4.11})^2 / (10^{-4} - 10^{-4.11}) = 2.69 \times 10^{-4}$$

$$3. \alpha = x/C_a = 10^{-4.11} / 10^{-4} = 0.776$$

### III- pH and degree of dissociation of weak bases

Consider a solution of weak base ( $B$  or  $B^-$ ) of concentration  $C_b$ .

The equilibrium of the reaction of this base with water is:



Where we let  $x = [\text{OH}^-]$  formed at equilibrium

$$\text{Acc. to SR. at eq : } n(\text{B})_{\text{reacted}} = n(\text{BH}^+)_{\text{formed}} = n(\text{OH}^-)_{\text{formed}}$$

By dividing by  $V_{\text{solution}}$  we obtain :  $[B]_{\text{reacted}} = [BH^+]_{\text{formed}} = [OH^-]_{\text{formed}} = x$

$$[B]_{\text{rem}} = [B]_0 - [B]_{\text{reacted}} = C_b - x$$

The equilibrium constant of this reaction is designated by  $K_b$  (basicity constant) :

$$K_b = \frac{[BH^+] \times [OH^-]}{[B]_{rem}} = \frac{x^2}{C_b - x} = \text{constant (given)}$$

By calculating  $x$ , we obtain  $[OH^-] = x$  calculated

$$x < C_b$$

The pH of the solution is :  $pH = 14 + \log [OH^-] = 14 + \log (x)$   $pH < 14 + \log C_b$

If the pH of the solution is known, we can calculate  $x$  directly :

$$x = [OH^-]_{\text{formed}} = 10^{(pH-14)}$$

The degree of dissociation  $\alpha$  of the weak base B is :

$$\alpha = \frac{n(B)_{\text{reacted}}}{n_0(B)} = \frac{[B]_{\text{reacted}}}{[B]_0} = \frac{x}{C_b} = \frac{10^{(pH-14)}}{C_b}$$

#### Note

In the case of strong bases :

$$[OH^-]_{\text{formed}} = C_b \text{ (complete reaction)}$$

$$pH = 14 + \log C_b$$

$$\alpha = 1 \text{ (100 %)}$$

The dilution 10 times decreases the pH one unit.

$$\alpha < 1 \text{ (in the case of weak bases)}$$

$$\alpha = x/C_b$$

### Effect of dilution on the pH and on $\alpha$ of weak bases

The dilution 10 times of solution of weak base will decrease its pH less than one unit.

#### Note

Each weak base (B) is characterized by its specific equilibrium constant  $K_b$  that is different to the other weak bases.

### Application 3

A solution of ammonia ( $NH_3$ ) having a concentration  $C_b = 5 \times 10^{-3} \text{ mol/L}$

1. Write the equation of the reaction of this base with water.
2. Determine the pH of the solution knowing that the equilibrium constant of this base is  $K_b = 1.584 \times 10^{-5}$
3. Deduce the degree of dissociation  $\alpha$  of this base.

#### Answer



Where  $x = [OH^-]_{\text{formed at equilibrium}}$

$$K_b = \frac{x^2}{5 \times 10^{-3} - x} = 1.584 \times 10^{-5} \quad x^2 + 1.584 \times 10^{-5}x - 7.924 \times 10^{-8} = 0$$

We solve the equation we find :  $x_1 = 2.73 \times 10^{-4}$  accepted

$$x_2 = -2.89 \times 10^{-4} \text{ rejected}$$

$$pH = 14 + \log x = 10.43$$

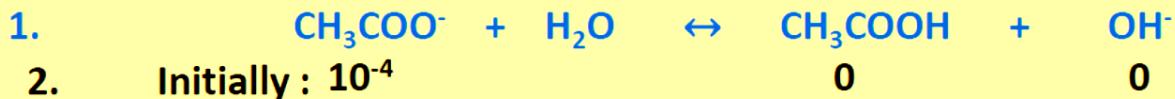
$$3. \alpha = \frac{n(NH_3)_{\text{reacted}}}{n_0(NH_3)} = \frac{x}{C_b} = \frac{(2.73 \times 10^{-4})}{5 \times 10^{-3}} = 0.0546 \text{ (5.46%)}$$

#### Application 4

A solution of sodium ethanoate ( $\text{Na}^+ + \text{CH}_3\text{COO}^-$ ) of concentration  $C_b = 10^{-4}$  mol/L having a pH = 7.37

1. Write the equation of the reaction of this weak base with water.
2. Determine the equilibrium constant  $K_b$  of this reaction.

#### Answer



At equilibrium:  $10^{-4} - x$   $x$   $x$

Where  $x = [\text{OH}^-]_{\text{formed at equilibrium}} = 10^{(\text{pH}-14)} = 10^{(7.37-14)} = 2.34 \times 10^{-7}$  mol/L

$$K_b = \frac{[\text{CH}_3\text{COOH}] \times [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{10^{-4} - x} \\ = (2.34 \times 10^{-7})^2 / (10^{-4} - 2.34 \times 10^{-7}) = 5.5 \times 10^{-10}$$

#### IV- classification of acid/base pairs

The power of acids depends on  $[\text{H}_3\text{O}^+]_{\text{formed}}$  from the reaction of the acid with water :  $\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-$

$[\text{H}_3\text{O}^+]_{\text{formed}}$  depends on  $K_a$  : as  $K_a \uparrow$ ,  $[\text{H}_3\text{O}^+]_{\text{formed}} \uparrow$  and the power of acid  $\uparrow$

The power of bases depends on  $[\text{OH}^-]_{\text{formed}}$  from the reaction of the base with water:  $\text{B} + \text{H}_2\text{O} \leftrightarrow \text{BH}^+ + \text{OH}^-$

$[\text{OH}^-]_{\text{formed}}$  depends on  $K_b$  : as  $K_b \uparrow$ ,  $[\text{OH}^-]_{\text{formed}} \uparrow$  and the power of base  $\uparrow$

Each (acid/base) pair has a specific  $K_a$  (relative to its acid) and a specific  $K_b$  (relative to its base).

For each (acid/base) pair :  $K_a \times K_b = K_w = 10^{-14} = \text{constant}$  ( $K_a = \frac{10^{-14}}{K_b}$ )

The power of acid and of base of (acid/base) pairs vary inversely since as  $K_a$  increases,  $K_b$  decreases and vice versa.

Since  $K_a$ ,  $K_b$  and  $K_w$  has very small values, we use  $pK_a$ ,  $pK_b$  and  $pK_w$  instead of  $K_a$ ,  $K_b$  and  $K_w$  for simplicity

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

$$pK_w = -\log K_w = -\log (10^{-14}) = 14$$

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

$$K_b = 10^{-pK_b}$$

$$K_w = 10^{-pK_w} = 10^{-14}$$

$$pK_a + pK_b = pK_w = 14$$

### Example of (acid/base) pairs :

$$K_a \times K_b = K_w = 10^{-14}$$

$$pK_a + pK_b = 14$$

		Increasing power of bases		Increasing pK <sub>a</sub>
		$K_a$		
HF/F <sup>-</sup>		$6.8 \times 10^{-4}$		3.17
CH <sub>3</sub> COOH/CH <sub>3</sub> COO <sup>-</sup>		$1.77 \times 10^{-5}$		4.75
HClO/ClO <sup>-</sup>		$5 \times 10^{-8}$		7.3
NH <sub>4</sub> <sup>+</sup> /NH <sub>3</sub>		$6.3 \times 10^{-10}$		9.2
C <sub>6</sub> H <sub>5</sub> OH/C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>		$1.25 \times 10^{-10}$		9.9

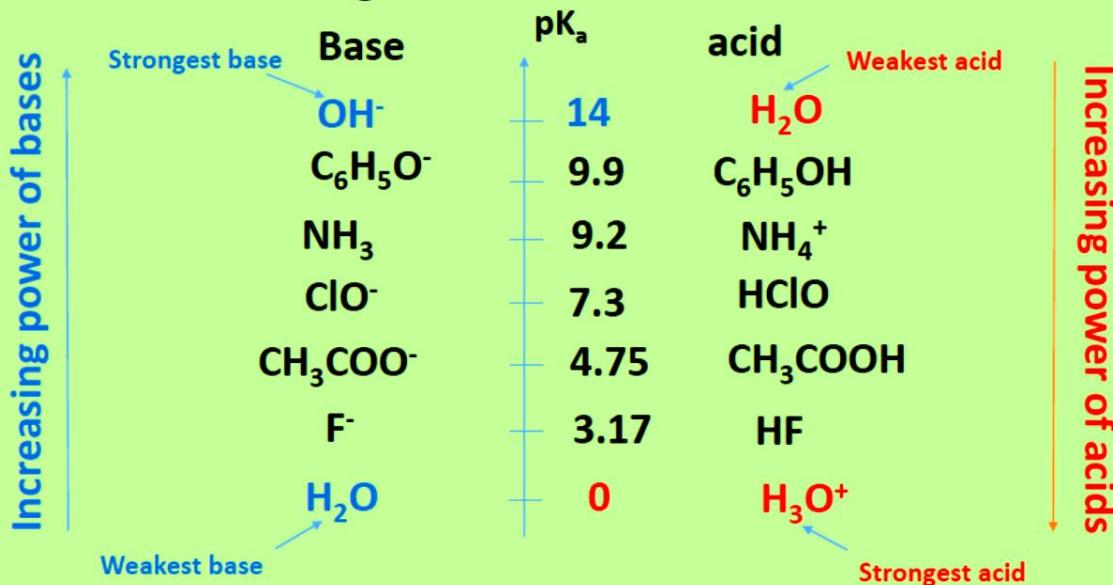
As  $K_a \uparrow$ ,  $pK_a \downarrow$ , the power of acids  $\uparrow$  and the power of bases  $\downarrow$

### Note:

The power of acids and of bases vary inversely since  $K_a$  and  $K_b$  vary inversely.

## Classification of (acid/base) pairs in a vertical axis of $pK_a$

The acid/base pairs are arranged in a vertical axis in increasing order of their  $pK_a$ , the **acids** are placed at **right side** and the **bases** are placed at the **left side** as the following :



### Note

The pair ( $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ ) is the pair relative to all strong acids (HCl,  $\text{HNO}_3$ , HBr)

The pair ( $\text{H}_2\text{O}/\text{OH}^-$ ) is the pair relative to all strong bases (NaOH, KOH, LiOH).

### V- reaction between two pairs and constant $K_R$ of the reaction

Between two pairs ( $\text{HA}_1/\text{A}_1^-$ ) and ( $\text{HA}_2/\text{A}_2^-$ ), two reactions are possible :

#### First reaction (gamma rule) :

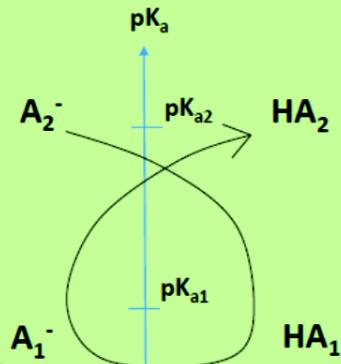


This reaction is **spontaneous** and it is considered as complete and quantitative if  $K_R > 10^4$

#### Second reaction (anti-gamma) :

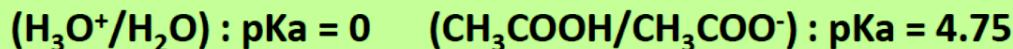


This reaction is **non spontaneous** and it is always **reversible**.

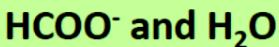
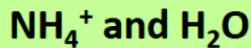
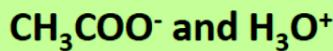


## Application 5

Consider the following acid/base pairs :



1. Arrange the above pairs in a vertical axis of pKa and indicate the increasing acidity and the increasing basicity.
2. Write the equation of each of the following reactions and deduce the constant  $K_R$  of each one :



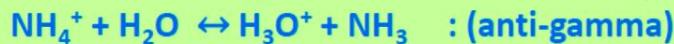
## Answer (application 5)

### 1. Vertical axis of pKa

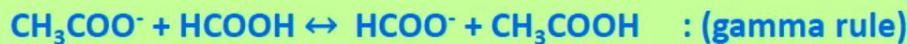
### 2. Reactions :



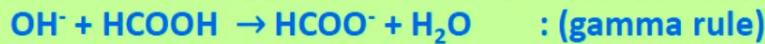
$$K_R = 10^{(4.75-0)} = 10^{4.75} > 10^4 \text{ (complete)}$$



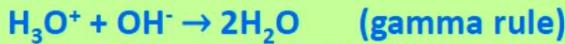
$$K_R = 10^{(0-9.2)} = 10^{-9.2} \ll 10^4 \text{ (incomplete)}$$



$$K_R = 10^{(4.75-3.75)} = 10 < 10^4 \text{ (incomplete)}$$



$$K_R = 10^{(14-3.75)} = 10^{10.25} > 10^4 \text{ (complete)}$$



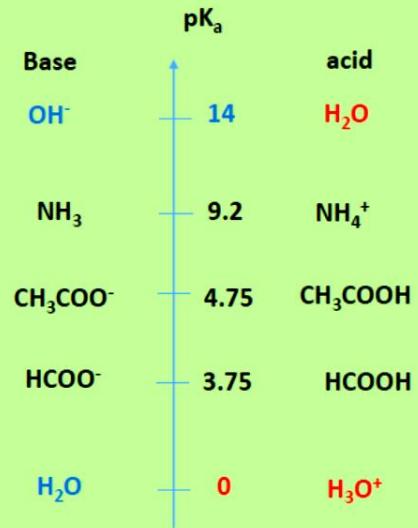
$$K_R = 10^{(14-0)} = 10^{14} \gg 10^4 \text{ (complete)}$$



$$K_R = 10^{(3.75-14)} = 10^{-10.25} \ll 10^4 \text{ (incomplete)}$$



$$K_R = 10^{(9.2-0)} = 10^{9.2} \gg 10^4 \text{ (complete)}$$



## V- Henderson relation – predominance domains of weak acid HA and of its conjugate base A<sup>-</sup>.

Consider the reaction of weak acid HA with water :



$$\text{The equilibrium constant } K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}]} = \frac{x^2}{c_a - x}$$

$$-\log K_a = -\log ([\text{H}_3\text{O}^+] \times \left( \frac{[\text{A}^-]}{[\text{HA}]_{\text{rem}}} \right))$$

$$\text{pK}_a = -\log [\text{H}_3\text{O}^+] - \log \left( \frac{[\text{A}^-]}{[\text{HA}]_{\text{rem}}} \right)$$

$$\text{pK}_a = \text{pH} - \log \left( \frac{[\text{A}^-]}{[\text{HA}]_{\text{rem}}} \right)$$

Handerson  
relation

$$\boxed{\text{pH} = \text{pK}_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)}$$

### Predominance domains of HA and of A<sup>-</sup>

Three cases are possible in a solution of weak acid and of weak base :

#### Case 1

If  $\text{pH}_{\text{solution}} = \text{pK}_a$  :  $[\text{HA}]_{\text{rem}} = [\text{A}^-]_{\text{formed}}$

No species predominates in the solution at this pH

#### Case 2

If  $\text{pH}_{\text{solution}} > \text{pK}_a + 1$  :  $[\text{A}^-]_{\text{formed}} > 10 \times [\text{HA}]_{\text{rem}}$

In this case A<sup>-</sup> predominates in the solution and HA is considered negligible.

#### Case 3

If  $\text{pH}_{\text{solution}} < \text{pK}_a - 1$  :  $[\text{HA}]_{\text{rem}} > 10 \times [\text{A}^-]_{\text{formed}}$

In this case HA predominates in the solution and A<sup>-</sup> is considered negligible.



## VI- Acid/base indicators

An acid base indicator is an acid/ base pair ( $\text{HA}/\text{A}^-$ ) having a given  $\text{pK}_a$  where the conjugate acid  $\text{HA}$  has a color different than that of its conjugate base  $\text{A}^-$ .

For example :  $\text{HA}$  has a yellow color and  $\text{A}^-$  has a blue color.

Three cases are possible :

### First case

If the indicator is placed in a solution having a  $\text{pH} < \text{pK}_a - 1$ , thus  $\text{HA}$  predominates in the solution and the color of the solution becomes yellow.

### Second case

If the indicator is placed in a solution having a  $\text{pH} > \text{pK}_a + 1$ , thus  $\text{A}^-$  predominates in the solution and the color of the solution becomes blue.

### Third case

If the indicator is placed in a solution having a pH that ranges between  $\text{pK}_a - 1$  and  $\text{pK}_a + 1$  ( $\text{pK}_a - 1 < \text{pH} < \text{pK}_a + 1$ ), thus  $[\text{HA}] \approx [\text{A}^-]$  and the color of solution is a mixture of yellow and blue (green).

## Examples of acid/base indicators

Indicators	pKa	Color of the acid species (HA)	pH change range	Color of the base species (A <sup>-</sup> )
Methyl orange	3.6	Red	3.1 – 4.4 Orange	Yellow
Methyl red	5.1	Red	4.2 – 6.2 Orange	Yellow
Bromothymol blue	6.8	Yellow	6 – 7.6 Green	Blue
Phenolphthalein	9		8.2 – 10 Pink	Purple

### Note about the neglecting of x as compared with C<sub>a</sub> or C<sub>b</sub>

Consider a solution of weak acid HA has a given C<sub>a</sub> and K<sub>a</sub>

$$K_a = \frac{x^2}{C_a - x} \quad (\text{where } x = [\text{H}_3\text{O}^+]_{\text{formed}})$$

If C<sub>a</sub> > 5 × 10<sup>-2</sup> mol.L<sup>-1</sup>, thus we can neglect x as compared with C<sub>a</sub> and the expression of K<sub>a</sub> becomes :

$$K_a = \frac{x^2}{C_a} \quad \text{therefore } x = \sqrt{K_a \times C_a}$$