

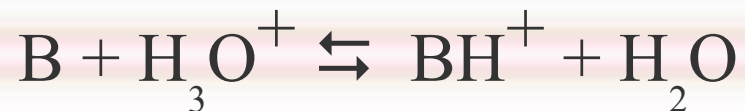
Acid and Basic compounds

A few definitions

- ◆ An **acid** compound is capable of releasing protons in solution



- ◆ A **basic** compound is capable either of binding free protons or of releasing hydroxyl ions



Relative strength of acids and bases

- ◆ In aqueous solutions, we can calculate the strength of acid and basic compounds with respect to their propensity of either donating or accepting protons from water
- ◆ The value of the equilibrium constant will tell us how strong is a compound with respect to water
- ◆ Water has both characteristics of an acid and of a base: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
- ◆ Its equilibrium constant at 25°C is

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

Relative strength of acids and bases

- ◆ Given that $K_w = 10^{-14}$, and given that the stoichiometric coefficients of protons and hydroxyls are equal \rightarrow

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

- ◆ Hence we can build a unit of measurements based on water's characteristics: the pH

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

- ◆ If the protons concentration in solution equals the hydroxyls concentration $\rightarrow \text{pH} = 7.0$
- ◆ If $[\text{H}_3\text{O}^+] > [\text{OH}^-] > 10^{-7} \text{ M} \rightarrow \text{pH} < 7.0$
- ◆ If $[\text{H}_3\text{O}^+] < [\text{OH}^-] < 10^{-7} \text{ M} \rightarrow \text{pH} > 7.0$

How can we calculate the pH value of a given solution?

- ◆ In case the solution contained a **strong acid**:



$$\rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log \mathbf{C}_a$$

- ◆ In case a solution contained a **strong base**:



$$\rightarrow \text{pOH} = -\log[\text{OH}^-] = -\log \mathbf{C}_b \quad \rightarrow \quad \text{pH} = 14 - \text{pOH}$$

How can we calculate the pH value of a given solution?

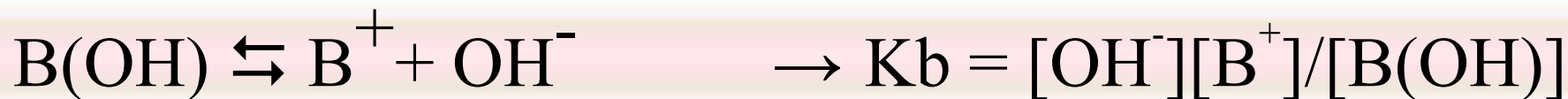
- ◆ In case a solution contained a weak **acid** ($K_a < 10^{-4}$)



$$\text{But } [\text{A}^-] = [\text{H}_3\text{O}^+] \rightarrow K_a = \frac{[\text{H}_3\text{O}^+]^2}{C_a}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_a} \rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+]$$

- ◆ In case a solution contained a weak **base** ($K_b < 10^{-4}$):



$$\rightarrow [\text{OH}^-] = \sqrt{K_b C_b} \rightarrow \text{pH} = 14 - \text{pOH}$$

Exercise 1

- ◆ Calculate the pH of a solution 0.02 M of $\text{Ba}(\text{OH})_2$.



This is a strong di-basic base \rightarrow the actual concentration of hydroxyl has to be calculated in Normality

$$[\text{OH}^-] = 2 \text{ Ca} = 2 \cdot 0.02 = 0.04 \text{ N}$$

$$\text{pOH} = -\log 0.04 = 1.4 \quad \rightarrow \quad \text{pH} = 14 - \text{pOH} = 14 - 1.4 = 12.6$$

Exercise 2

- ◆ Calculate K_a of a weak acid whose solution 0.1M has pH=4.

A generic weak acid will dissociate with the following equilibrium:



$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{C_a}$$

To convert pH into $[\text{H}_3\text{O}^+]$ we need the inverse formula of log:

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

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{C_a} = \frac{(10^{-4})^2}{0.1} = 10^{-7} \text{ M}$$

Exercise 3

- ◆ Calculate the pH of a solution of ammonia when there are 10^{-4} mol in 100 ml ($K_b = 1.8 \cdot 10^{-5}$ M)



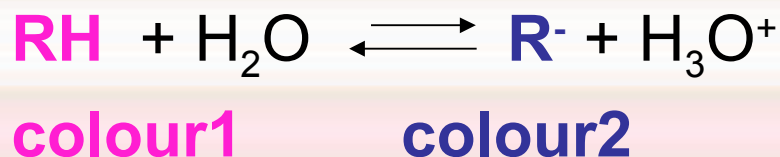
In a weak base $[\text{OH}^-] = \sqrt{K_b C_b}$

$$C_b = [\text{NH}_3] = 10^{-4} / 0.1 = 10^{-3} \text{ M}$$

$$[\text{OH}^-] = \sqrt{K_b \cdot C_b} = \sqrt{1.8 \cdot 10^{-5} \cdot 10^{-3}} = 1.34 \cdot 10^{-4} \text{ M}$$

$$\text{pOH} = -\log 1.34 \cdot 10^{-4} = 3.87 \quad \rightarrow \text{pH} = 14 - 3.87 = 10.13$$

pH indicators: halochromic detectors of protons



$$K = \frac{[\text{H}_3\text{O}^+][\text{R}^-]}{[\text{RH}]} \quad \rightarrow \quad [\text{H}_3\text{O}^+] = K \frac{[\text{RH}]}{[\text{R}^-]} \quad \rightarrow \quad \text{pH} = \text{pK} + \log \frac{[\text{R}^-]}{[\text{RH}]}$$

- ◆ In case the indicator is inside an acidic solution:
 - ◆ Proton concentration increases
 - ◆ The equilibrium moves leftwards
 - ◆ Colour 1 is abundant

- ◆ In case the indicator is inside a basic solution:
 - ◆ Proton concentration decreases
 - ◆ The equilibrium moves rightwards
 - ◆ Colour 2 is abundant

- ◆ In case $[\text{R}^-] = [\text{RH}] \rightarrow$ transition point \rightarrow the colour is intermediate between 1 and 2

Exercise 4

- ◆ A pH indicator RH with $K_{ind} = 10^{-6}$ M, is red when indissociated and yellow once dissociated. Which is the colour when it is added to a solution 0.1 M of ethanoic acid? ($K_a = 1.8 \cdot 10^{-5}$ M)



$$K_{ind} = \frac{[\text{R}^-][\text{H}_3\text{O}^+]}{[\text{RH}]}$$

The pH of the solution is:

$$\text{pH} = -\log \sqrt{K_a C_a} = -\log \sqrt{1.8 \cdot 10^{-5} \cdot 0.1} = -\log 1.34 \cdot 10^{-3} = 2.87$$

$$\frac{[\text{RH}]}{[\text{R}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{ind}} = \frac{1.34 \cdot 10^{-3}}{10^{-6}} = 1340 \quad \rightarrow \text{the solution is } \mathbf{RED}$$

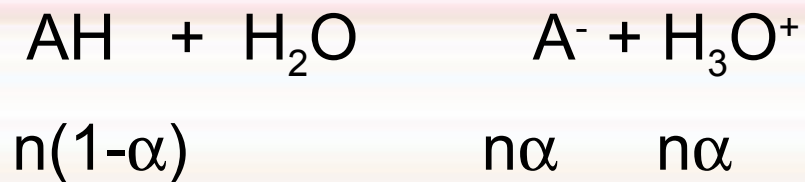
As a general rule:

pH < pKind \rightarrow colour of the indissociated species

pH > pKind \rightarrow colour of the dissociated species

Exercise 5

- ◆ A 0.1 M solution of a weak monoprotic acid has the same pH of a solution 10^{-4} of HCl. Calculate the dissociation coefficient of the weak acid.



$$\text{pH}_{\text{ac.}} = \text{pH}_{\text{.HCl}} = 4$$

$$[\text{H}_3\text{O}^+]_{\text{ac.}} = [\text{H}_3\text{O}^+]_{\text{sol.HCl}} = 10^{-4}\text{M}$$

$$[\text{H}_3\text{O}^+] = \text{Ca} \cdot \alpha \quad \rightarrow \quad \alpha = [\text{H}_3\text{O}^+] / \text{Ca} = 10^{-4} / 0.1 = 10^{-3}$$

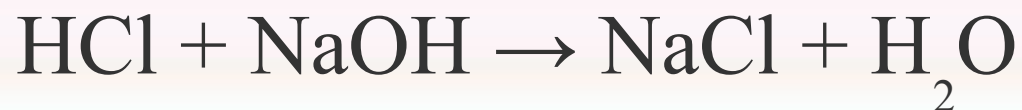
Basic / acidic Hydrolysis

- ◆ Salts are strong electrolytes, completely dissociated into ions once in water
- ◆ The dissociated ions maintain the chemical behaviour of their precursor
- ◆ Hence if they were issued from either weak acids or weak bases they tend to set up an equilibrium at the expenses of water
- ◆ We define hydrolysis the chemical reaction during which molecules of water (H_2O) are split into protons and hydroxide anions

The behaviour of salts formed by a strong acid reacting with a strong base



We can think of sodium chloride as originated from the neutralization reaction:



In water, the solid compound is completely dissociated into ions, which are stable in their configuration \rightarrow they do not react with water
 $\rightarrow \text{pH} = 7$

The behaviour of salts formed by a weak acid reacting with a strong base



- ◆ The acetate anion set up an equilibrium with water, by perturbing this latter's equilibrium
- ◆ This new equilibrium is called eq. of hydrolysis a constant can be calculated: $K_i = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$
- ◆ In solution there is also water's proper equilibrium:
 $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \rightarrow [\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$

$$K_i = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

We can substitute OH^- in the above formula to obtain:

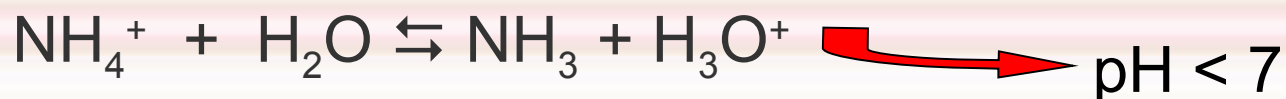
$$K_i = \frac{[CH_3COOH]K_w}{[CH_3COO^-][H_3O^+]} \quad K_i = \frac{K_w}{K_a}$$

We can also calculate the pH of this salt, starting from K_i :

$$K_i = \frac{[CH_3COOH] \cdot [OH^-]}{[CH_3COO^-]} = \frac{[OH^-]^2}{C_s}$$

$$pOH = -\log \sqrt{(K_w \cdot C_s) / K_a}$$

The behaviour of salts formed by a weak base reacting with a strong acid



- ◆ Even in this case we can calculate a K_i and rearrange it by taking into account water's equilibrium:

$$K_i = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \qquad K_i = \frac{K_w}{K_b}$$

- ◆ We can also calculate the pH:

$$K_i = \frac{[\text{H}_3\text{O}^+]^2}{C_s} \quad \rightarrow \quad [\text{H}_3\text{O}^+] = \sqrt{K_w \cdot C_s / K_b}$$

Exercise 1

- ◆ Calculate the concentration of HCN and the pH of a solution 0.2 M of KCN ($K_a = 4 \cdot 10^{-10}$ M)



$$[\text{OH}^-] = \sqrt{(K_w \cdot C_s) / K_a} = \sqrt{(10^{-14} \cdot 0.2 / 4 \cdot 10^{-10})} = 2.2 \cdot 10^{-3} \text{ M}$$

$$[\text{HCN}] = [\text{OH}^-] = 2.2 \cdot 10^{-3} \text{ M}$$

$$\text{pOH} = 2.65 \rightarrow \text{pH} = 14 - \text{pOH} = 11.35$$

Exercise 2

- ◆ An aqueous solution of ammonium chloride has pH= 5. Calculate the molar concentration of the salt, given that $K_b = 1.8 \cdot 10^{-5}$ M.



$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5}\text{M} = \sqrt{(\text{K}_w \cdot \text{C}_s) / \text{K}_b}$$

$$\rightarrow \text{C}_s = [\text{H}_3\text{O}^+] \cdot \text{K}_b / \text{K}_w = (10^{-5})^2 \cdot 1.8 \cdot 10^{-5} / 10^{-14} = 0.18 \text{ M}$$

Exercise 3

- ◆ Calculate the pH of a $5 \cdot 10^{-3}$ M solution of potassium methanoate ($K_a = 2 \cdot 10^{-4}$ M)



$$[\text{OH}^-] = \sqrt{K_w \cdot C_s / K_a} = \sqrt{(10^{-14} \cdot 5 \cdot 10^{-3} / 2 \cdot 10^{-4})} = 4.47 \cdot 10^{-7}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 6.35 = 7.65$$