Equilibrium pt.2
acids and bases

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Class Goals

- Review of concept of acid and base
- Apply equilibrium for weak acid/base
- Calculate pH at equilibrium

Chemical Equilibrium

Some reaction develop until completion, i.e. combustion

Other reactions just develop to some extension → part of the reagent does not react

↓

These reaction is said that reached the
CHEMICAL EQUILIBRIUM

Example: weak acid or base

Le Chatelier's principle

A change in one of the variables that describe a system at equilibrium produces a shift in the position of the equilibrium that counteracts the effect of this change.

The system adjust to maintain the Kc value

More reagents or product can appear, but the proportion remains the same

Changing the amounts

Perturbation	Effect
Reagent addition	$A + B \xrightarrow[\text{direct}]{} C + D$
Reagent removal	$A + B \xleftarrow[\text{inverse}]{} C + D$
Product Addition	$A + B \xleftarrow[\text{inverse}]{} C + D$
Product removal	$A + B \xrightarrow[\text{direct}]{} C + D$

Changing the temperature

We need to know that exists reaction that:

- Release heat: they are called **Exothermic**
- Require heat: they are called **Endothermic**

❖ **Endothermic** Reaction: heat is considered as a **reagent**

$$A + B + q \rightleftarrows C + D$$

❖ **Exothermic** Reaction: heat is considered as a **product**

$$A + B \rightleftarrows C + D + q$$

Changing the pressure

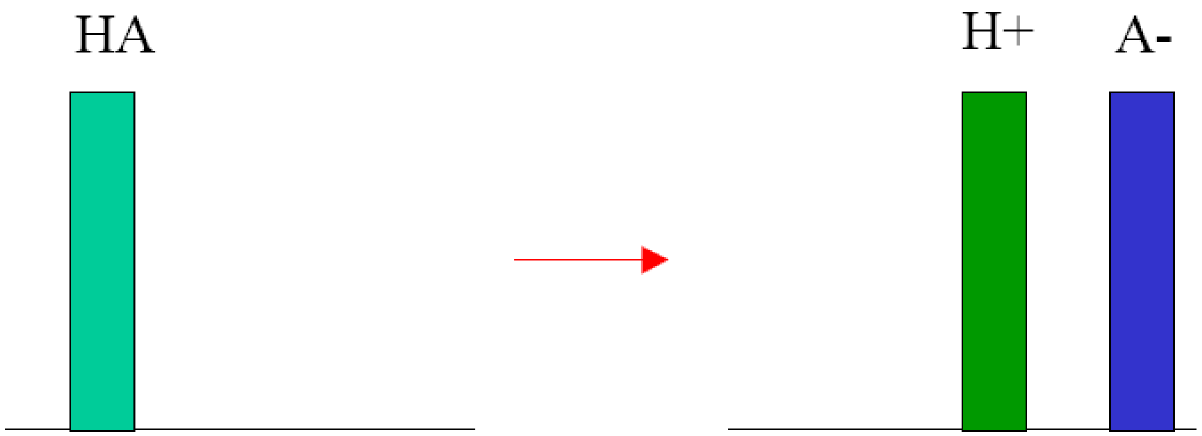
Changing the pressure affects only reagent and products that are in a GAS state.

The total pressure within the reaction vessel depends on the **number of molecules of gas** in the container.

If the **pressure is increased**, Le Chatelier's Principle states that the reaction will counter this by shifting the equilibrium to favor the side with **fewer molecules**.

If the **pressure is decreased**, the reaction will try to favor the side with **more molecules**.

Chemical Equilibrium

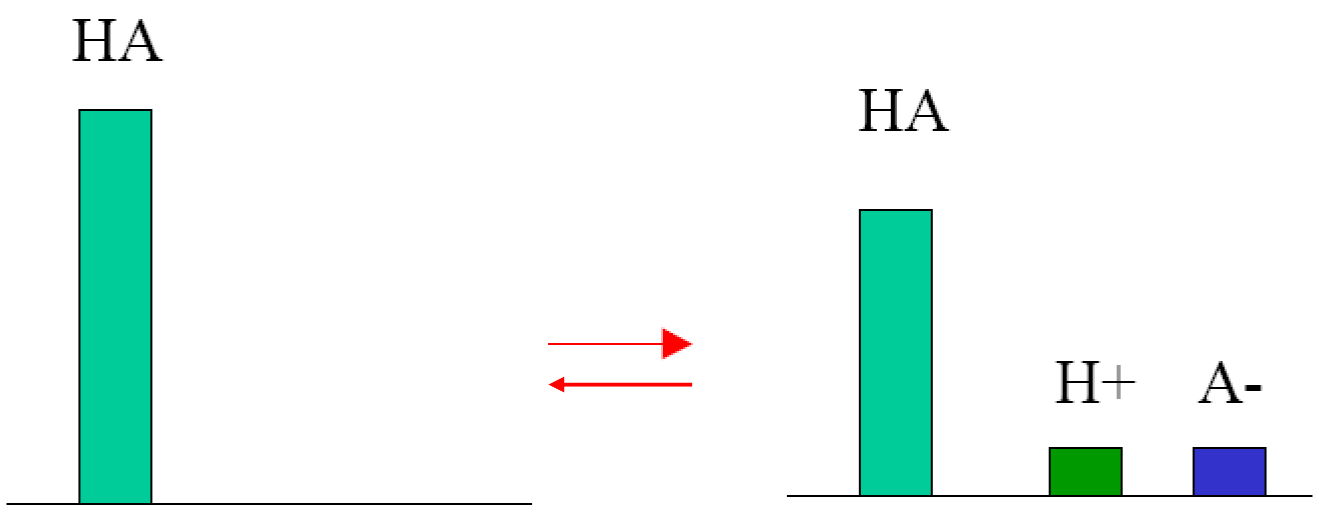


Strong acid/base:

Complete reaction, only product at the end

Weak acid/base:

Partial reaction, leftover of reagent at the end

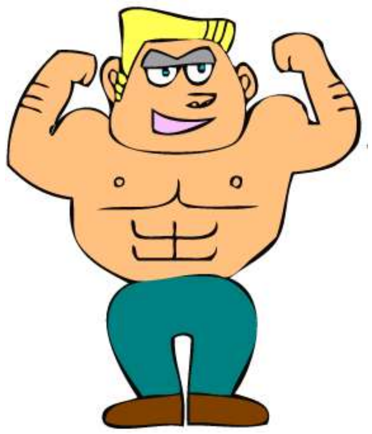


Strong acid/base

1. Inorganic acid: HNO_3, $HClO_4$, *H_2SO_4, HCl, HI, HBr,

2. Alkali metal and alkali-earth metal **hydroxides**

*H_2SO_4 only the first dissociation is complete. The second dissociation is partial, so HSO_4^- is a weak acid



Calculations: strong acid/base

I have 250mL of a solution of chloric acid, HCl, at 0.5 M. What is the concentration of H^+ ions?

I have 125mL of a solution of $Ba(OH)_2$, what is the concentration of (OH^-) ions? What is the pH?

pH scale

To avoid very small number, we take the **negative logarithm** of the concentration:

Ex:

$[H^+] = 1,0 \times 10^{-5}$

pH= **-log** $[H^+]$ = -log $[10^{-5}] = +5$

pH scale

[H+]	pH	[OH-]	pOH
1	0	1×10^{-14}	14
1×10^{-1}	1	1×10^{-13}	13
1×10^{-2}	2	1×10^{-12}	12
1×10^{-3}	3	1×10^{-11}	11
1×10^{-4}	4	1×10^{-10}	10
1×10^{-5}	5	1×10^{-9}	9
1×10^{-6}	6	1×10^{-8}	8
1×10^{-7}	7	1×10^{-7}	7
1×10^{-8}	8	1×10^{-6}	6
1×10^{-9}	9	1×10^{-5}	5
1×10^{-10}	10	1×10^{-4}	4
1×10^{-11}	11	1×10^{-3}	3
1×10^{-12}	12	1×10^{-2}	2
1×10^{-13}	13	1×10^{-1}	1
1×10^{-14}	14	1	0

acid

neutral

basic

OBSERVATIONS:

✓ **pH + pOH is Always equal to 14**

Why ?

Because of the water dissociation constant !!

$$H_20 \leftrightarrows H^+ + OH^-$$

$$K_w = [H^+]\,[OH^-] = 10^{-14}$$

$[H^+] \times [OH^-]$ is always equal to 10^{-14}

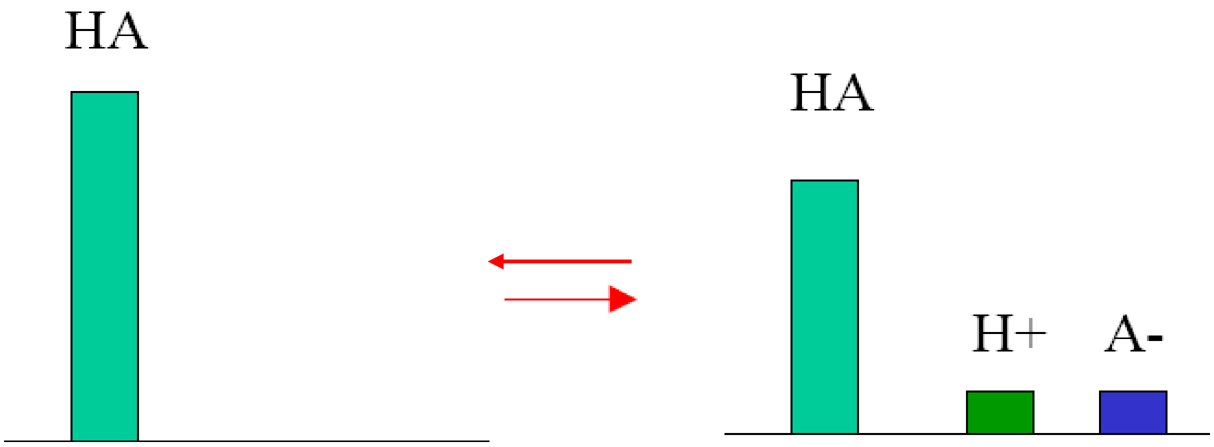
Weak acid/base

Weak

1. Inorganic acids like H_2CO_3, H_3PO_4, H_2S
2. Organic acid (formic acid);
3. Ammonia (NH_3) and most of organic bases;

In this case, the concentration of H^+ or OH^- depends on the equilibrium → we need an equilibrium constant, $\mathbf{K_c}$

Chemical Equilibrium



Important concepts:

The amounts of reagents and product at the equilibrium is **NOT** the same

TWO reactions are occurring at the same time:

- reagents to product: direct reaction
- products back to reagents: inverse reaction

Reversible reaction

Equilibrium constant for acid

If we consider the equilibrium of a general acid HA:

$HA \leftrightarrows H^+ + A^-$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

$HA + H_2O \leftrightarrows H_3O^+ + A^-$

The equilibrium constant K_a is the DISSOCIATION constant of the weak acid.

Equilibrium constant for base

Same reasoning can be applied with bases:

$$BOH \leftrightarrows B^{+} + OH^{-}$$

$$K_b = \frac{\left[B^{+}\right]\left[OH^{-}\right]}{\left[BOH\right]}$$

The equilibrium constant K_b is the DISSOCIATION constant of the weak base.

Equilibrium dissociation constant

I can use it to classify the strenght of a weak acid or base.
So I can compare diferente acids/bases

higher K_a → higher dissociation of H^+ → more acid

higher K_b → higher dissociation of OH^- → more basic

Dissociation constants at 25C

Acid	Formula	K_1	K_2	K_3
Acetic acid	CH_3COOH	1.75×10^{-5}		
Ammonium ion	NH_4^+	5.70×10^{-10}		
Anilinium ion	$C_6H_5NH_3^+$	2.51×10^{-5}		
Arsenic acid	H_3AsO_4	5.8×10^{-3}	1.1×10^{-7}	3.2×10^{-12}
Arsenous acid	H_3AsO_3	5.1×10^{-10}		
Benzoic acid	C_6H_5COOH	6.28×10^{-5}		
Boric acid	H_3BO_3	5.81×10^{-10}		
1-Butanoic acid	$CH_3CH_2CH_2COOH$	1.52×10^{-5}		
Carbonic acid	H_2CO_3	4.45×10^{-7}	4.69×10^{-11}	
Chloroacetic acid	$ClCH_2COOH$	1.36×10^{-3}		
Citric acid	$HOOC(OH)C(CH_2COOH)_2$	7.45×10^{-4}	1.73×10^{-5}	4.02×10^{-7}
Dimethyl ammonium ion	$(CH_3)_2NH_2^+$	1.68×10^{-11}		
Ethanol ammonium ion	$HOC_2H_4NH_3^+$	3.18×10^{-10}		
Ethyl ammonium ion	$C_2H_5NH_3^+$	2.31×10^{-11}		
Ethylene diammonium ion	$^+H_3NCH_2CH_2NH_3^+$	1.42×10^{-7}	1.18×10^{-10}	
Formic acid	$HCOOH$	1.80×10^{-4}		
Fumaric acid	*trans*-HOOCCH:CHCOOH	8.85×10^{-4}	3.21×10^{-5}	
Glycolic acid	$HOCH_2COOH$	1.47×10^{-4}		
Hydrazinium ion	$H_2NNH_3^+$	1.05×10^{-8}		
Hydrazoic acid	HN_3	2.2×10^{-5}		
Hydrogen cyanide	HCN	6.2×10^{-10}		

Conjugated acid/base

If we write this reaction

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

Conjugated acid/base

If we write this reaction

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We need to keep in mind that actually two reactions are occurring:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$ Direct reaction

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$ Inverse reaction

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A weak base generates a weak acid: it's called conjugated acid.

A weak acid generates a weak base: it's called a conjugated base.

Conjugated acid/base

If we write this reaction

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

We need to keep in mind that actually two reactions are occurring:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \boxed{K_b}$$

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+ \qquad \boxed{K_a}$$

K_b and K_a from conjugated acid/base are called conjugated constant.

Relationship of Conjugated constants

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

Relationship of Conjugated constants

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

$$K_a = \frac{\left[NH_3\right]\left[H_3O^+\right]}{\left[NH_4^+\right]}$$

Relationship of Conjugated constants

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$NH_4^+ + NH_3 + 2H_2O \leftrightarrows NH_4^+ + OH^- + NH_3 + H_3O^+$$

$$Kc = \frac{[NH_4^+][OH^-]}{[NH_3]} \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Relationship of Conjugated constants

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$NH_4^+ + NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- + NH_3 + H_3O^+$

$$Kc = \frac{[NH_4^+][OH^-]}{[NH_3]}\frac{[NH_3][H_3O^+]}{[NH_4^+]} = [H_3O^+] x [OH^-] = K_\omega$$

Water dissociation constant

Relationship of Conjugated constants

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$NH_4^+ + NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- + NH_3 + H_3O^+$$

$$Kc = \frac{[NH_4^+][OH^-]}{[NH_3]}\frac{[NH_3][H_3O^+]}{[NH_4^+]} = [H_3O^+] x [OH^-] = K_\omega$$

Important Information

1. If we combine two or more reaction happening at the same time, the final equilibrium constant is the multiplication of each individual equilibrium constant.
(this is true for all reactions)

2. The multiplication of K_a with K_b of a conjugated pair of weak acid/base is always equal to 10^{-14}

Exercise

The K_b value for the ammonia reaction is: 1.8×10^{-5}

$$\mathbf{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

How much is the K_a for the conjugated acid NH_4^+ ?

= [$5{,}7 \times 10^{-10}$]

More on constants

We saw that:

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

This might be a complicated number, but we can do like for pH: the minus logarithm of this number!

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

$pK_a + pK_b = 14$ very similar to $pH + pOH = 14$

Equilibrium dissociation constant

I can use it to classify the strenght of a weak acid or base.
So I can compare diferente acids/bases

higher Ka → higher dissociation of H^+ → more acid

higher Kb → higher dissociation of OH^- → more basic

BE CAREFUL !

Equilibrium dissociation constant

higher Ka → higher dissociation of H^+ → more acid

higher Kb → higher dissociation of OH^- → more basic

however

less pKa → more acid !

it's the opposite !!

less pKb → more basic !

Calculating pH with weak acid

Consider the generic reaction:

$$\underset{\text{Weak Acid}}{HA_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Conjugated base}}{A^-_{(aq)}}$$

At equilibrium:

$$K_A = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

What is the concentration of H_3O^+ ?

$\longrightarrow$ I.C.E. Table !!

from ICE Table

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Weak Acid — Conjugated base

At equilibrium: $[H_3O^+] = [A^-] = x$

K_a pode ser escrita como: $K_A = \dfrac{[H_3O^+]\,[A^-]}{[HA]} = \dfrac{[H_3O^+]^2}{[HA]}$

$\Rightarrow [H_3O^+]^2 = K_a\,[HA]$

from ICE Table

K_a pode ser escrita como:

$$K_a = \frac{[H_3O^+]^2}{[HA]} \Rightarrow [H_3O^+]^2 = K_a [HA]$$

Initial acid concentration: C_A (mol L^{-1}):

At equilibrium, the concentraion of the acid will be:

$$[HA] = C_A - [H^+]$$

equilibrium

initial

$$[H_3O^+]^2 = K_a\,[HA] = K_a(C_A - H^+)$$

$$[H^+]^2 + K_a[H^+] - K_aC_A = O$$

$$\downarrow$$

$$\boxed{x^2 + K_ax - K_aC_A = O}$$ → Equação de segundo grau em H^+

but when $C_A >>> K_a$ → $\boxed{[H^+] = \sqrt{C_A K_a}}$

from ICE Table

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

when $C_A >>> K_a$

$$\frac{C_A}{K_A} > 10^4 > 10{,}000$$

condition to simplify

$$[H^+] = \sqrt{C_A K_a}$$

much easier !!

Calculating pH with weak acid

Exercise: Calcule the concentration of H_3O^+ in a solution of 1.20 mol L^{-1} of nitrous acid, following this reaction:

$$\mathbf{HNO_2 + H_2O \leftrightarrows H_3O^+ + NO_2^-}$$

$K_a = 7{,}1 \times 10^{-6}$

Calculating pH with weak acid

Exercise: Calcule the concentration of H_3O^+ in a solution of 1.20 mol L^{-1} of nitrous acid, following this reaction:

$$\mathbf{HNO_2 + H_2O \leftrightarrows H_3O^+ + NO_2^-}$$

$Ka = 7.1 \times 10^{-6}$

$$\frac{C_A}{K_A} > 10^4 \xrightarrow{\text{yes!}} [H^+] = \sqrt{C_A K_a}$$

Solving, we have:

$[H_3O^+] = 2.91 \times 10^{-3}$ mol L^{-1}

$pH = -\log [H_3O^+] = 2.53$

Calculating pH with weak base

With bases we need to calculate **pOH** and then transform to pH.

Same formula!

$$\boxed{[OH^-] = \sqrt{C_B K_b}}$$

Check if → $\dfrac{C_B}{K_b} > 10^4$

calculate pOH ⟶

pH + pOH = 14

pH = 14 - pOH

Calculating pH with weak base

Exercise: Calculate the concentration of OH^- from a solution of 0.750 mol L^{-1} of ammonia (NH_3).

$$\mathbf{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

$K_{a\ NH4+} = 5.70 \times 10^{-10}$

Calculating pH with weak base

Exercise: Calculate the concentration of OH^- from a solution of 0.750 mol L^{-1} of ammonia (NH_3).

$$\mathbf{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

$K_{a\ NH4+}$ = 5,70 x 10^{-10}

If I work with base I need K_b!!

1. $K_b = K_w/K_a \rightarrow K_b = \dfrac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} \rightarrow K_b = 1.75 \times 10^{-5}$

2. Check if $\dfrac{C_B}{K_b} > 10^4$

3. $[OH^-] = \sqrt{C_B K_b} \Rightarrow$ $\mathbf{[OH^-] = 1.15 \times 10^{-3}\ mol\ L^{-1}}$

Calculating pH with weak base

Exercise: Calculate the concentration of OH^- from a solution of 0.750 mol L^{-1} of ammonia (NH_3).

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \qquad K_{a\ NH4+} = 5.70 \times 10^{-10}$$

...

$$\Rightarrow \quad [OH^-] = 1.15 \times 10^{-3} \text{ mol } L^{-1}$$

4. $[OH^-] = 1.15 \times 10^{-3}$ mol L^{-1} $\Rightarrow$ $pOH = 2.94$

5. $pH = 14 - pOH$ $\qquad pH = 11.06$

Calculating pH with weak base

Exercise: The acid dissociation constant (K_a) for benzoic acid is 6.3×10^{-5}. Find the pH of a 0.35 M solution of benzoic acid.

pH = 2.33

Calculating pH with weak base

Exercise: Calculate the concentration of OH^- from a solution of 0.340 mol L^{-1} of ammonia (NH_3).

$$\mathbf{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

$K_{a\ NH4+} = 5.70 \times 10^{-10}$

pH = 11.40

Salt hydrolysis

What happens in we have multiple substances in a solution that can affect pH ?

Sometimes when I put salt in water, weak acids or bases can be formed.

Example

Sodium acetate: $CH_3COONa_{(s)} \leftrightarrows CH_3COO^-_{(aq)} + Na^+_{(aq)}$

but

$$\underbrace{CH_3COO^-_{(aq)}}_{\text{it's a weak base}} + H_2O_{(l)} \leftrightarrows CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Salt hydrolysis

What happens in we have multiple substances in a solution that can affect pH ?

Sometimes when I put salt in water, weak acids or bases can be formed.

Example 2

Ammonium chloride: $NH_4Cl_{(s)} \leftrightarrows NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

but

$$\underbrace{NH_4^+{}_{(aq)}}_{\text{it's a weak acid}} + H_2O_{(l)} \leftrightarrows NH_{3(aq)} + H_3O^+{}_{(aq)}$$

Salt hydrolysis

When salts are dissolved in water, not always we have a neutral solution.

Salt dissociation $NH_4Cl \leftrightarrows NH_4^+ + Cl^-$

base equilibrium $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

Salt hydrolysis

When salts are dissolved in water, not always we have a neutral solution.

Salt dissociation $NH_4Cl \leftrightarrows \cancel{NH_4^+} + Cl^-$

acid equilibrium $\cancel{NH_4^+} + H_2O \leftrightarrows NH_3 + H_3O^+$

global reaction $\mathbf{NH_4Cl + H_2O \leftrightarrows NH_3 + Cl^- +} H_3O^+$

The resulting solution is acidic.

Exercise

What is the pH of a solution that is 2.5 M NaCN? $K_{a\,(HCN)} = 4.9 \times 10^{-10}$

Exercise

What is the pH of a solution that is 2.5 M NaCN? $K_{a\,(HCN)} = 4.9 \times 10^{-10}$

	$CN^-(aq)$ +	$H_2O(l)$	$\rightleftarrows HCN(aq)$ +	$OH^-(aq)$
I	2.5 M		0	0
C	- x		+x	+x
E	2.5 M - x		x	x

Assume x is neglible and 2.5 M – x ≅ 2.5 M

$$\frac{x^2}{2.5} = 4.9 \times 10^{-10}$$

Always check if you can use this formula

$$x = \sqrt{2.5 \times (4.9 \times 10^{-10})} = 3.5 \times 10^{-5}\ M$$

pH = 14.00 – (-log(3.5 x 10^{-5}) = **9.54**

Salt hydrolysis

When salts are dissolved in water, not always we have a neutral solution.

Salt dissociation $$CH_3COONa_{(s)} \leftrightarrows CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

base equilibrium $$CH_3COO^- + H_2O_{(l)} \leftrightarrows CH_3COOH + OH^-$$

Salt hydrolysis

When salts are dissolved in water, not always we have a neutral solution.

Salt dissociation $$CH_3COONa_{(s)} \leftrightarrows \cancel{CH_3COO^-}_{(aq)} + Na^+_{(aq)}$$

base equilibrium $$\cancel{CH_3COO^-} + H_2O_{(l)} \leftrightarrows CH_3COOH + OH^-$$

global reaction $$CH_3COONa_{(s)} + H_2O_{(l)} \leftrightarrows CH_3COOH_{(aq)} + OH^- + Na^+$$

The resulting solution is basic.

Salt hydrolysis

What happens if the salt is made by a weak acid and a weak base ions?

Ammonium acetate: NH_4AOc

Salt dissociation $$NH_4OAc \leftrightarrows NH_4^+ + OAc^-$$

+

weak acid dissociation $$NH_4^+ \leftrightarrows NH_3 + H^+$$

+

weak base dissociation $$OAc^- + H_2O \leftrightarrows HOAc + OH^-$$

How can we know if the final solution is acid or basic?

Salt hydrolysis

We need to compare the K_a and K_b.

If $K_a > K_b$, the solution will be acid

If $K_a < K_b$, the solution will be basic

If $K_a \cong K_b$, the solution will be neutral

or

If $pK_a < pK_b$, the solution will be acid

If $pK_a > K_b$, the solution will be basic

If $pK_a \cong pK_b$, the solution will be neutral

Exercise

What is the pH of a solution of 0.50M of ammonium acetate (NH_4AOc) ?

$K_{a\ NH4+} = 5.70 \times 10^{-10}$

$K_{b\ OAc-} = 5.60 \times 10^{-10}$

Exercise #2

What is the pH of a solution of 0.50M of ammonium hipochlorite (NH_4ClO) ?

$K_{a\ NH4+} = 5.70 \times 10^{-10}$

$K_{b\ ClO-} = 3.45 \times 10^{-7}$

Exercise #2

What is the pH of a solution of 0.50M of ammonium hipochlorite (NH_4ClO) ?

$K_{a\ NH4+} = 5.70 \times 10^{-10}$

$K_{b\ ClO-} = 3.45 \times 10^{-7}$

Exercise

This salt is going to form a weak acid solution or a weak basic solution ?

a) Na_2CO_3

b) $KHSO_4$

d) $CsBr$