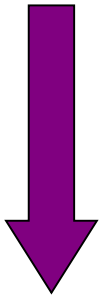
EQUILÍBRIOS IÔNICOS

Eletrólitos

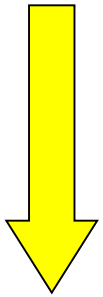
Fortes



Ionizam/Dissociam completamente

Ex: HCl, $NaNO_3$

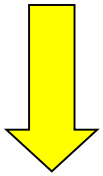
Fracos



Ionizam/Dissociam parcialmente

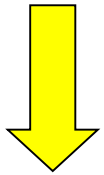
Ex: HF, $BaSO_4$

Fracos

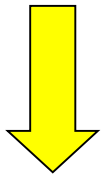


Ionizam/Dissociam

Parcialmente



Extensão do
Processo Parcial



Processo em Equilíbrio

EQUILÍBRIOS ÁCIDO-BASE

AUTO-IONIZAÇÃO DA ÁGUA

$H_2O\ (l) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + OH^-\ (aq)$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

H_2O = Líquido puro (a=1) /concentração constante

$$K_W = [H_3O^+][OH^-]$$

forma simplificada

$$K_W = [H^+][OH^-]$$

$[H_3O^+] = [OH^-] = 1{,}0 \times 10^{-7}\ mol.L^{-1}$

25ºC

$K_W = [H_3O^+][OH^-] = 1{,}0 \times 10^{-14}\ mol.L^{-1}$

T (°C)	K_W
0	1.1×10^{-15}
10	2.9×10^{-15}
25	1.0×10^{-14}
37*	2.4×10^{-14}
45	4.0×10^{-14}
60	9.6×10^{-14}

Classificação soluções ácido-base:

Solução	Condição	25 ºC	
ácida	$[H_3O^+] > [OH^-]$	$[H_3O^+] > 1x10^{-7}$	$[OH^-] < 1x10^{-7}$
neutra	$[H_3O^+] = [OH^-]$	$[H_3O^+] = 1x10^{-7}$	$[OH^-] = 1x10^{-7}$
básica	$[H_3O^+] < [OH^-]$	$[H_3O^+] < 1x10^{-7}$	$[OH^-] > 1x10^{-7}$

Escala de pH e pOH

$pH = -\log[H_3O^+]$ → $[H_3O^+] = 10^{-pH}$

$pOH = -\log[OH^-]$ → $[OH^-] = 10^{-pOH}$

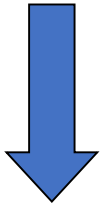
$H_2O(l)$ → $pH = 7,0$

$H_2O(l)$ → $pOH = 7,0$

$$K_W = [H_3O^+][OH^-] = 1{,}0 \times 10^{-14}$$

$$-\log K_W = -\log([H_3O^+][OH^-])$$

$$-\log K_W = -\log([H_3O^+] + (-\log[OH^-])$$



$$pK_W = pH + pOH = 14{,}00$$

Dissolução de Ácidos ou Bases Fortes e K_W

Solução aquosa 0,05 *M* HNO_3

- $[H_3O^+]$= ?
- $[OH^-]$= ?

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

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

$1x10^{-7}$ M

0,05 M

$[H_3O^+]= 1x10^{-7} + 0,05 \approx 0,05$

$K_W = [H_3O^+][OH^-] = 1,0x10^{-14}\ mol.L^{-1}$

$K_W = [0,05][OH^-] = 1,0x10^{-14}\ mol.L^{-1}$

$[OH^-] = 2,0x10^{-13}\ mol.L^{-1}$

Solução 0,015 *M* $Ba(OH)_2$

$[H_3O^+]$=? $[OH^-]$=? pH=? pOH=?

$Ba(OH)_2 \rightarrow Ba^{+2} + 2\ OH^-$

$[OH^-]$= 2x0,015= 0,030

pOH= -log[0,030]= -(-1,52)= 1,52

pH + pOH= 14,00

pH + 1,52= 14,00

pH= 12,48

$[H_3O^+][OH^-] = 1,0x10^{-14}$

$[H_3O^+][0,03] = 1,0x10^{-14}$

$[H_3O^+] = 3,33x10^{-13}$ *M*

Ácidos e Bases Fracas

Ácidos

Quais são fortes?

HCl, HBr, HI, HNO_3 $HClO_4$ e H_2SO_4 (apenas 1ª ionização)

Bases

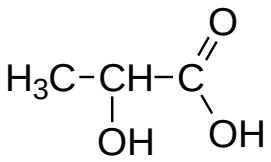
Quais são fortes?

Hidróxidos 1A: LiOH, NaOH, KOH, RbOH, CsOH

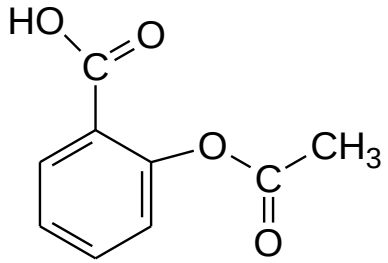
Hidróxidos 2A: $Sr(OH)_2$ e $Ba(OH)_2$

Ácidos Fracos:

Praticamente todos os demais inorgânicos e os carboxílicos.

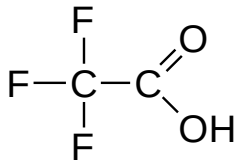


Ac. Lático



Ac. Acetilsalicílico

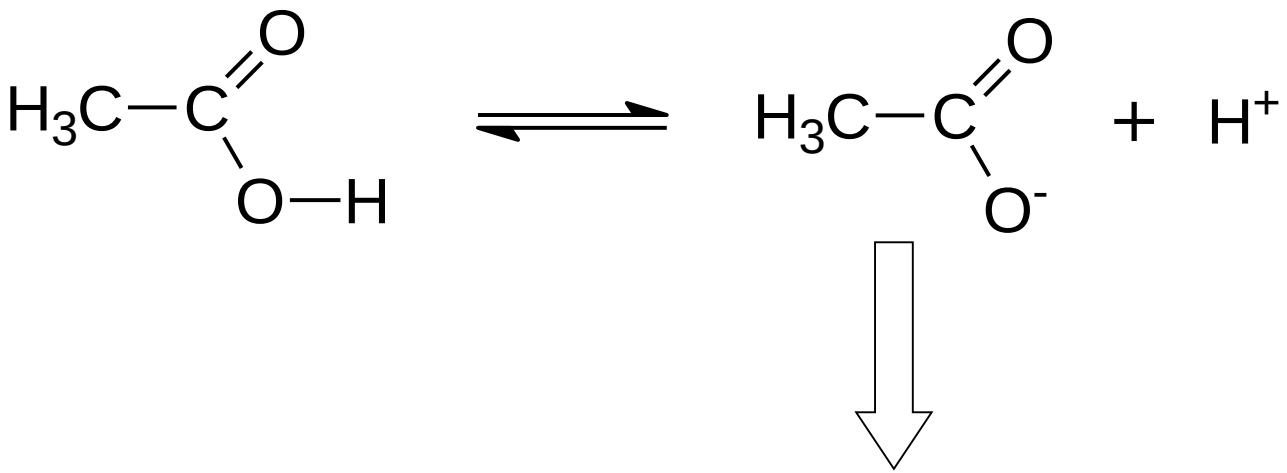
Exceções, pex:



Trifluor acético

Moderado

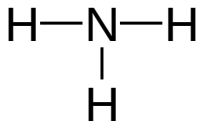
Ionização Ácido Carboxílico



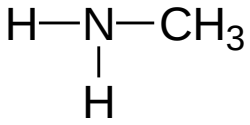
Ânion Carboxilato

Bases Fracas:

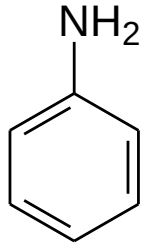
Praticamente todos os demais hidróxidos metálicos e as aminas.



amônia



metil-amina



anilina

Ácido Fraco → $[H_3O^+]$ $(10^{-2} - 10^{-7})$

pH ≈ 2 - 7

Base Fraca → $[OH^-]$ $(10^{-2} - 10^{-7})$

pH ≈ 12 - 7

K_a e K_b

$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$

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

$pK_a = -\log K_a$

$CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1{,}8x10^{-5}$$

$$K = \frac{[H_3O^+][Ac^-]}{[HAc]} = 1{,}8x10^{-5}$$

$B(aq) + H_2O(l) \leftrightarrows BH^+(aq) + OH^-(aq)$

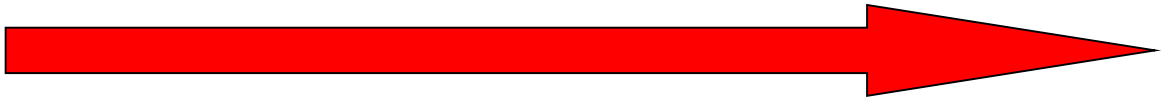
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$pK_b = -\log K_b$

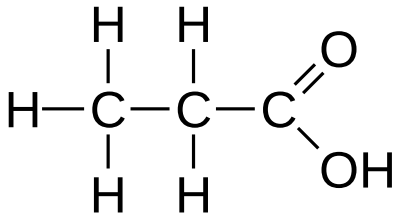
$NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$

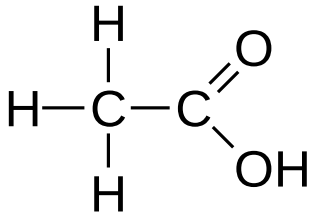
$$K = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1{,}8x10^{-5}$$

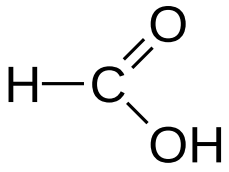
Acidez Aumenta



Propanóico **Acético** **Fórmico**







K_a	$1,3x10^{-5}$	$1,8x10^{-5}$	$1,8x10^{-4}$
pK_a	4,89	4,74	3,74

pK_a Diminui

Ácidos Polipróticos

$H_3PO_4 + H_2O \leftrightarrows H_3O^+ + H_2PO_4^-$ $K_{a1} = 7{,}5 \times 10^{-3}$

$H_2PO_4^- + H_2O \leftrightarrows H_3O^+ + HPO_4^{2-}$ $K_{a2} = 6{,}2 \times 10^{-8}$

$HPO_4^{2-} + H_2O \leftrightarrows H_3O^+ + PO_4^{3-}$ $K_{a3} = 3{,}6 \times 10^{-13}$

Bases *"Polipróticas"*

$CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + OH^-$ $\quad K_{b1} = 2{,}1 \times 10^{-4}$

$HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^-$ $\quad K_{b2} = 2{,}4 \times 10^{-8}$

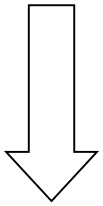
pH de Soluções Salinas/Hidrólise/Solvólise

$HX + H_2O \leftrightarrows H_3O^+ + X^-$

Ácido forte → $K_A >> 1$ → $K_B << 1$ → X^-: Base + Fraca (H_2O)

$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$ → Base muito fraca

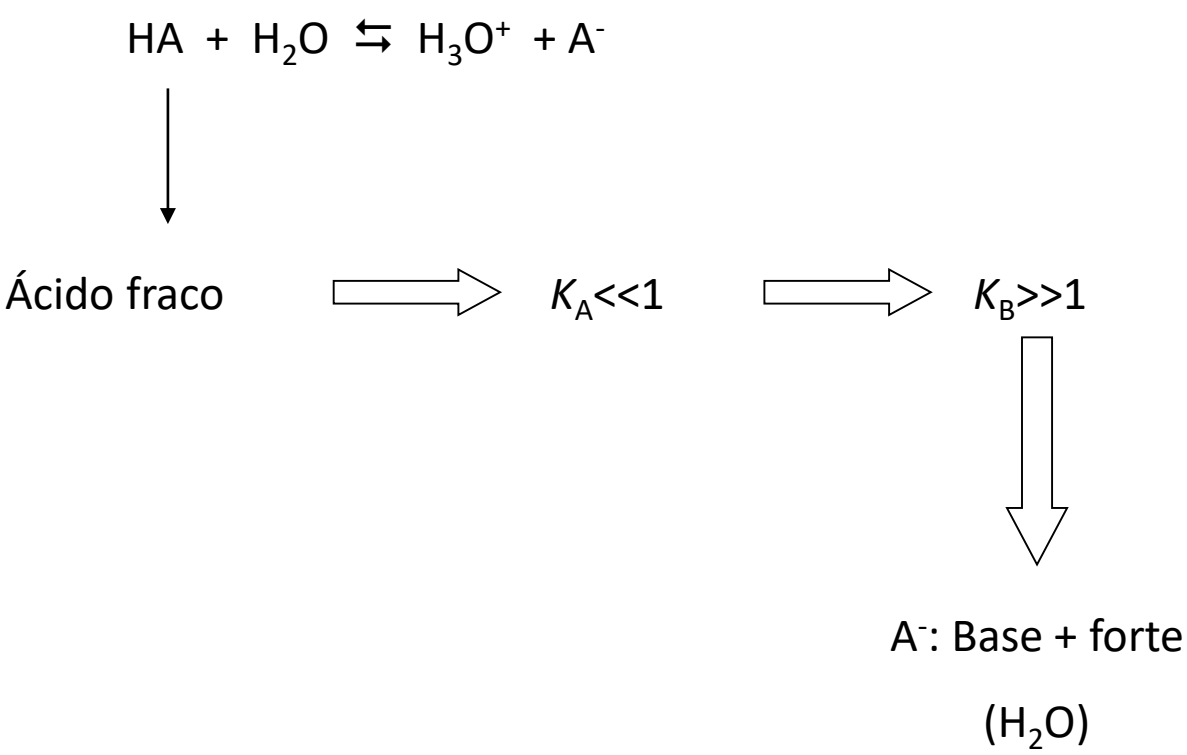
$NaCl(aq) \longrightarrow Cl^-(aq) + H_2O \rightarrow$ X

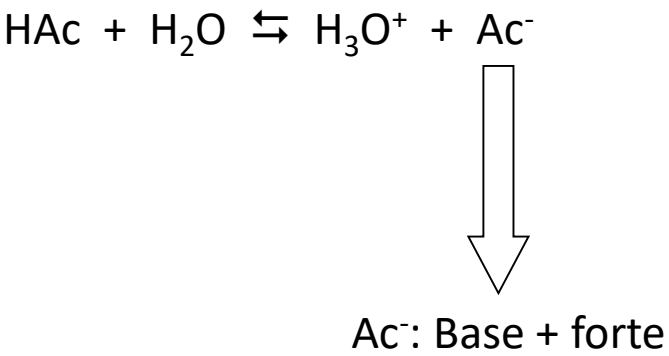


Não Ocorre

$K_W = [H^+][OH^-] = [1x10^{-7}][1x10^{-7}]$

pH= pOH= 7


HA + H2O ⇆ H3O+ + A-
Ácido fraco
KA<<1
KB>>1
A-: Base + forte
(H2O)


HAc + H2O ⇆ H3O+ + Ac-
Ac-: Base + forte

$NaAc(aq) \longrightarrow Ac^-(aq) + H_2O \rightarrow ???$

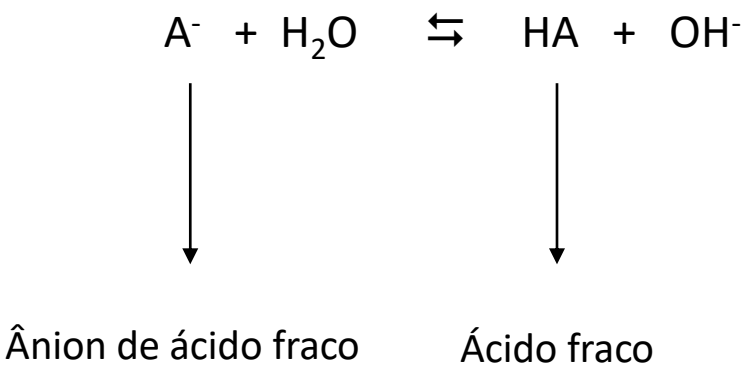
$Ac^- + H_2O \rightarrow HAc + OH^-$

Ácido fraco

$K_W = [H^+][OH^-] = [<1x10^{-7}][>1x10^{-7}]$

pH>7 pOH<7

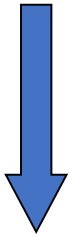
pH de Soluções Salinas/Hidrólise/Solvólise



pH de Soluções Salinas/Hidrólise/Solvólise

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

Base fraca  $K_B<<1$  $K_A>>1$



NH_4^+: Ácido + forte

(H_2O)

$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

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

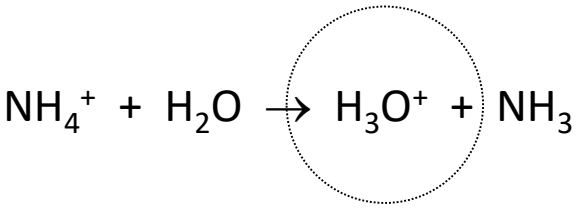
Base fraca

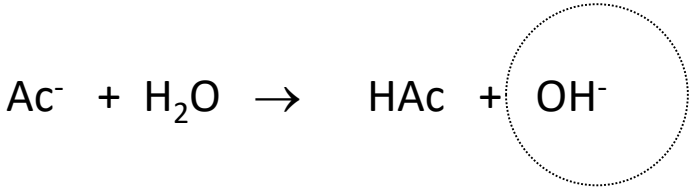
$K_W = [H^+][OH^-] = [>1x10^{-7}][<1x10^{-7}]$

pH<7 pOH>7

pH de Soluções Salinas/Hidrólise/Solvólise

E o que ocorre com NH_4Ac???????





pH depende dos valores de K_A e K_B

Relacionando K_A com K_B da base conjugada

$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$

Base conjugada

$$K_A = \frac{[H_3O^+][CN^-]}{[HCN]}$$

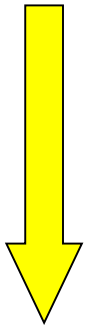
$CN^- + H_2O \leftrightarrows HCN + OH^-$

$$K_B^{CN^-} = \frac{[OH^-][HCN]}{[CN^-]}$$

$$K_A x K_B^{CN^-} = \frac{[H_3O^+][CN^-]}{HCN} x \frac{[OH^-][HCN]}{[CN^-]}$$

$$K_A x K_B^{CN^-} = [H_3O^+][OH^-] = K_W$$

Efeito do Íon Comum



Sistemas Tampão

Cálculo $[\ ]_{EQ}$ Ácido Fraco:

HAc 0,100 M (K_A= 1,8x10^{-5})

	HAc	+	H_2O ⇆	H_3O^+	+	Ac^-
In	0,1000			--		---
	-x			+x		+x
Eq:	0,100-x			+x		+x

$$K_A = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{(x)(x)}{(0{,}100 - x)} = \frac{x^2}{0{,}100 - x} = 1{,}8x10^{-5}$$

Supondo x<<<0,10 ⟶ 0,10-x= 0,10

$$\frac{x^2}{0{,}100} = 1{,}8x10^{-5}$$

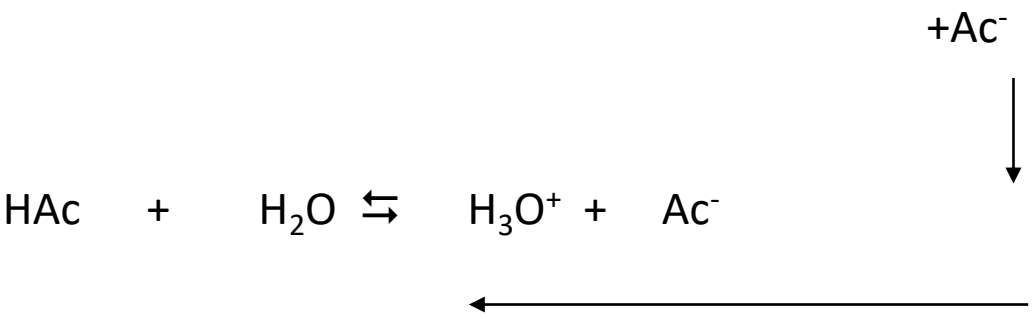
$$x^2 = 1{,}8x10^{-6} = x = \sqrt{1{,}8x10^{-5}} = 1{,}3x10^{-3}\,M$$

Para: 0,100-0,0013= 0,0987≈ 0,099 ≈ 0,100

E se a concentração inicial de HAc fosse 0,00250 M?????

Efeito do Íon Comum

Princípio de Le Chatelier aplicado soluções iônicas



Solução 0,10M HAc + 0,10M NaAc

	HAc	+	H_2O ⇆	H_3O^+	+	Ac^-
In	0,10			--		---
	-x			+x		+x
Eq:	0,10-x			+x		0,10+x

$$K_A = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{(x)(0{,}10+x)}{(0{,}100-x)} = x = 1{,}8x10^{-5}$$

$[H_3O^+]$= 1,8x10^{-5} M

$[Ac^-]$= 0,10 M

Tampão

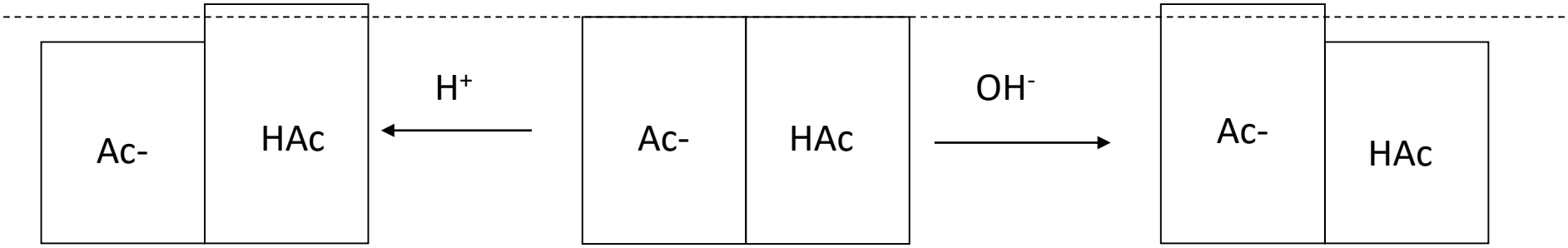
1) Componente que neutralize ácidos

2) Componente que neutralize bases

Os componentes entre si não podem se neutralizar

Tampão

- Um ácido fraco e sua base conjugada
- Uma base fraca e seu ácido conjugado



pH de soluções tampão

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

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

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

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

pK_A pH

$$pK_A = pH - \log \frac{[A^-]}{[HA]}$$

$$pH = pK_A + \log \frac{[A^-]}{[HA]}$$

Equação de Henderson-Hasselbach

$$pH = pK_A + \log \frac{[Base\,Conjugada]}{[Ácido]}$$

Sistema HAc/Ac^-
- pK_A^{HAc}
- [Ac^-] do sal
- [HAc]

Sistema NH_3/NH_4^+
- p$K_A^{NH_4^+}$
- [NH_3] da base conjugada
- [NH_4^+] do sal

Condições para o efeito tampão

[base conjugada]/[ácido] 0,1 ⇔ 10

[HA] e [A^-] > 100xK_A

c-x≈ c

Condições para o efeito tampão

[base conjugada]/[ácido] 0,1 ⇔ 10

[HA] e $[A^-] > 100 \times K_A$

$c - x \approx c$