Diagramme de prédominance

HA/A⁻

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

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

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

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

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

- Cas 1 : $[A^-] = [HA]$

$\frac{[A^-]}{[HA]} = 1 \Rightarrow \log\frac{[A^-]}{[HA]} = \log(1) = 0$

$$pH = pK_a$$

Cas 2 : $[HA] > [A^-]$

$\frac{[A^-]}{[HA]} < 1 \Rightarrow \log\frac{[A^-]}{[HA]} < \log(1) < 0$

on ajoute pK_a

$$pK_a + \log\frac{[A^-]}{[HA]} < pK_a$$

$$pH < pK_a$$

Cas 3 : $[HA] < [A^-] \Rightarrow \frac{[A^-]}{[HA]} > 1$

$\log\frac{[A^-]}{[HA]} > \log(1) = 0$

on ajoute $pK_a \Rightarrow \underbrace{pK_a + \log\frac{[A^-]}{[HA]}}_{pH} > pK_a$

$$pH > pK_a$$

$[HA] > [A^-]$ Acide — $[A^-] = [HA]$ — Base

prédominant $pH = pK_a$ prédominant pH

- Espèces majoritaire et minoritaire

$[HA]/A^-$, $HA + H_2O \rightleftharpoons A^- + H_3O^+$

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

$-\log$ Joie

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

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

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

Cas 1 : Acide majoritaire

$[HA] >>> [A^-] \Rightarrow [HA] \geq 10[A^-]$

$\frac{[A^-]}{[HA]} \leqslant \frac{1}{10} \leqslant 10^{-1}$ inverse

$\log\frac{[A^-]}{[HA]} \leqslant \log(10^{-1})$

: pK_a ajoute

$pK_a + \log\frac{[A^-]}{[HA]} \leqslant pK_a - 1$

$pH \leqslant pK_a - 1$

$[HA] >> [A^-]$ — $pK_a - 1$ — $pH = pK_a$

Acide majoritaire

$[HA] + [A^-]$

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base majoritaire ✓

$[A^-] \gg [HA] \Rightarrow [A^-] \geq 10[HA]$

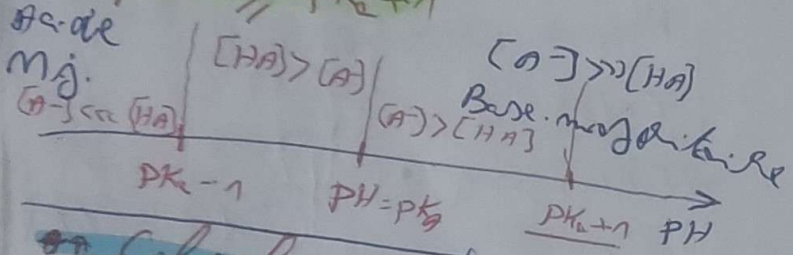
$\frac{[A^-]}{[HA]} \geq 10$

$\log \frac{[A^-]}{[HA]} \geq \log(10) = 1$

pK_a de

$pK_a + \log \frac{[A^-]}{[HA]} \geq pK_a + 1$

$pH \geq pK_a + 1$



Calcul de pH

1) pH d'un acide fort: C_0

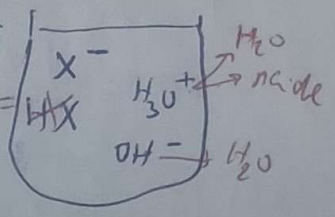
(HX, C_0)

$HX + H_2O \longrightarrow X^-$ (base forte) $+ H_3O^+$

Totalement dissocié

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

$\alpha \simeq 1$ coef dissociation



Hypothèse:

1- Electroneutralité (ENS):

$\sum [X_i]^+ = \sum [X_i]^-$

$[H_3O^+] = [X^-] + [OH^-]$ ... (1)

2) Conservation de la matière (C.M.)

$C_0 \leftarrow HX + H_2O \longrightarrow X^- + H_3O^+$

$C_0 = [HX] + [X^-]$ ... (2)

Totalement dissocié

(2) dans (1):

$[H_3O^+] = C_0 + [OH^-]$ ... (1)

3- $K_e = [H_3O^+][OH^-]$

$\Rightarrow [OH^-] = \frac{K_e}{[H_3O^+]}$ ... (3)

On remplace (3) dans (1):

$[H_3O^+] = C_0 + \frac{K_e}{[H_3O^+]}$

$[H_3O^+]^2 = C_0[H_3O^+] + K_e$

$[H_3O^+]^2 - C_0[H_3O^+] - K_e = 0$

Eq. de 2ème ordre: $x^2 - bx + c = 0$

$\Delta = C_0^2 + (4.1.K_e) = C_0^2 + 4K_e > 0$

$\Delta = b^2 - 4ac$ $\quad x_1 = \frac{-b + \sqrt{\Delta}}{2a}$ ↗ +

(+) $[H_3O^+] = \frac{C_0 + \sqrt{C_0^2 + 4K_e}}{2}$

$pH = -\log \frac{C_0 + \sqrt{C_0^2 + 4K_e}}{2}$

C_0 est très faible

Remarque:

1- Si: $C_0 > 10^{-6,5}$ M $\Rightarrow [H_3O^+] \gg [OH^-]$ milieu acide

On: $[H_3O^+] = C_0 + [OH^-]$ ... (1)

(1) $\Rightarrow [H_3O^+] = C_0$

donc: $pH = -\log C_0$

milieu acide $pH \leq 6,5$

c) Calcul du pH

2) pH d'un acide faible (HA, C_0, pK_a)

faiblement dissocié.

α : coeff de dissociation < 1

$$\alpha = \frac{[A^-]}{C_0}$$

faible = $RCOOH$ + [illegible]

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

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

H_3O^+	OH^-
reste HA	A^-

Les équations :

1) E.N.S : $\Sigma [X_n]^+ = \Sigma [X_n]^-$

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

Dans les milieux acide $pH \leq 6{,}5$

2) C.M. : $C_0 = [HA] + [A^-]$

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

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

(ENS) $\Rightarrow$ $$K_a = \frac{[H_3O^+]\cdot[H_3O^+]}{C_0 - [A^-]}$$

$[HA] \to$ C.M

$$K_a = \frac{[H_3O^+]^2}{C_0 - [A^-]}$$

$$K_a = \frac{[H_3O^+]^2}{C_0 - [H_3O^+]}$$

si : $pK_a + \log C_0 \geq 2$

~~si : $pK_a + \log C_0 < 2$~~

إذا كان ما تحققش نعوضوا من الدرجة 2

faible : $[H_3O^+]^2 = K_a C_0 - K_a [H_3O^+]$

$$[H_3O^+]^2 + K_a [H_3O^+] - K_a \cdot C_0 = 0$$

éq. 2ème degrée :

$$\Delta = b^2 - 4ac = K_a^2 + 4K_aC_0$$

$$x = \frac{-b + \sqrt{\Delta}}{2}$$

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_0}}{2}$$

$$pH = -\log\left(\frac{-K_a + \sqrt{K_a^2 + 4K_aC_0}}{2}\right)$$

$pH \leq 6{,}5$

Remarque

Si : $pK_a + \log(C_0) \geq 2$ $\left(\frac{K_a}{C_0} \leq 10^{-2}\right)$

$[HA] \ggg [A^-] \Rightarrow C_0 \ggg [H_3O^+]$

On a : $$K_a = \frac{[H_3O^+]^2}{C_0 - [H_3O^+]}$$

$$[H_3O^+]^2 = K_a \cdot C_0$$

$$[H_3O^+] = (K_a \cdot C_0)^{1/2}$$

$$pH = -\log[H_3O^+] = -\frac{1}{2}\log(K_a \cdot C_0)$$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C_0$$

pH Base Fort :

Base forte : Totalement dissociée
$\alpha = 1$

$$BOH \xrightarrow{H_2O} B^+ + OH^-$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+$$

B^+	H_3O^+
OH^-	BOH

1) ENS : $[B^+] + [H_3O^+] = [OH^-]$ ...(1)

2) C.M :
$C_0 = [B^+] + [BOH]$ ...(2)
$\Rightarrow C_0 = [B^+]$.

(2) dans (1) : $[OH^-] = C_0 + [H_3O^+]$ ...(1')

3) $K_e = [OH^-] \cdot [H_3O^+] \Rightarrow [H_3O^+] = \frac{K_e}{[OH^-]}$ ...(3)

(3) dans (1') :
$$[OH^-] = C_0 + \frac{K_e}{[OH^-]}$$
$$[OH^-]^2 = C_0[OH^-] + K_e$$
$$[OH^-]^2 - C_0[OH^-] - K_e = 0.$$
$$\Delta = C_0^2 + 4K_e > 0. \quad (\Delta = b^2 - 4ac)$$
$$[OH^-] = \frac{C_0 + \sqrt{C_0^2 + 4K_e}}{2}$$
$$pOH = -\log[OH^-] = -\log\left(\frac{C_0 + \sqrt{C_0^2 + 4K_e}}{2}\right)$$
$$pH = 14 - pOH$$
$$pH = 14 + \log\left(\frac{C_0 + \sqrt{C_0^2 + 4K_e}}{2}\right)$$

Remarque : Si : $C_0 \geq 10^{-6}$ M
$[OH^-] = [B^+] = C_0$ ... $[OH^-] \ggg [H_3O^+]$.
$pOH = -\log C_0 \Rightarrow pH = 14 + \log C_0 \rightarrow pH \geq 7$ ✓

pH d'une Base Faible :

(B, C_0, K_B)

$K_A \cdot K_B = K_e$
$pK_A + pK_B = 14$

faiblement dissociée

$$\alpha = \frac{[Acide]}{C_0} \Rightarrow \alpha < 1$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
$$2H_2O \rightleftharpoons OH^- + H_3O^+$$

OH^-	BH^+
H_3O^+	B

1) ENS :
$[OH^-] = [BH^+] + [H_3O^+]$ (pH ≥ 7.5)

2) C.M : $[B] + [BH^+] = C_0$

$$K_B = \frac{[BH^+][OH^-]}{[B]} = \frac{[OH^-]^2}{C_0 - [BH^+]}$$

$$K_B = \frac{[OH^-]^2}{C_0 - [OH^-]}$$
$$[OH^-]^2 + K_B[OH^-] - K_B C_0 = 0$$
$$\Delta = b^2 - 4ac = K_B^2 + 4K_B \cdot C_0 > 0$$
$$[OH^-] = \frac{-K_B + \sqrt{K_B^2 + 4K_B C_0}}{2}$$
$$pOH = -\log\left[\frac{-K_B + \sqrt{K_B^2 + 4C_0 K_B}}{2}\right]$$
$$pH = 14 - pOH$$
$$pH = 14 + \log\left[\frac{-K_B + \sqrt{K_B^2 + 4C_0 K_B}}{2}\right]$$
pH ≥ 7 ✓

Remarque : Si $pK_B + \log C_0 \geq 2$
où $\frac{K_B}{C_0} \leq 10^{-2} \Rightarrow [B] \ggg [BH^+]$

$$K_B = \frac{[OH^-]^2}{C_0}$$
$$[OH^-] = \sqrt{K_B C_0} = (K_B \cdot C_0)^{1/2}$$

Remarque : Si : $pK_B + \log C_0 \geq 2$

on : $\frac{K_B}{C_0} \leq 10^{-2}$

$\Rightarrow [B] >>> [BH^+]$.

On a : $K_B = \frac{[OH^-]^2}{C_0 - [BH^+]}$

$[OH^-]^2 = K_B \cdot C_0 \Rightarrow [OH^-] = \sqrt{K_B \cdot C_0} = (K_B C_0)^{1/2}$

$-\log[OH^-] = -\frac{1}{2}(\log(K_B) + \log(C_0))$

$pOH = -\frac{1}{2}\log K_B - \frac{1}{2}\log(C_0)$.

$pH = 14 - pOH$

$pH = 14 + \frac{1}{2}\log(K_B) + \frac{1}{2}\log C_0$

$pH = 14 - \frac{1}{2}pK_B + \frac{1}{2}\log(C_0)$

$$pH = 14 - \frac{1}{2}pK_B + \frac{1}{2}\log(C_0)$$

$pK_A + pK_B = 14$

$pH = 14 - \frac{1}{2}(14 - pK_A) + \frac{1}{2}\log C_0$

$pH = 14 - 7 + \frac{1}{2}pK_A + \frac{1}{2}\log C_0$

$$pH = 7 + \frac{1}{2}pK_A + \frac{1}{2}\log C_0$$

pH d'un Acide - Acide fort

1) Acide fort (HX_1, C_1, V_1) + Acide fort$_2$ (HX_2, C_2, V_2)

$HX_1 + H_2O \longrightarrow X_1^- + H_3O^+$

$HX_2 + H_2O \longrightarrow X_2^- + H_3O^+$

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

Mélange ~~$+A, C_1 = C$~~

$C_1' = \frac{C_1 \cdot V_1}{V_1 + V_2}$

$C_2' = \frac{C_2 \cdot V_2}{V_1 + V_2}$

X_1^-	H_3O^+
X_2^-	OH^-

ENS : $[H_3O^+] = [OH^-] + [X_1^-] + [X_2^-]$ ...(1)

C.M$_1$: ~~$[HX_1]$~~ $+ [X_1^-] = C_1'$ ...(2)

C.M$_2$: $\alpha = 1$ ~~$[HX_2]$~~ $+ [X_2^-] = C_2'$ ...(3)

(2) et (3) dans (1) $\Rightarrow [H_3O^+] = (C_1') + (C_2')$

$pH = -\log[H_3O^+] = -\log(C_1' + C_2')$

$$pH = -\log(C_1' + C_2')$$

* Mélange Acide fort et faible :

(HX_1, C_1, V_1) (HX_2, C_2, V_2, K_A)

Conclusion : A. fort + A. faible

pH = pH d'un acide fort.

$C_1' = \frac{C_1 \cdot V_1}{V_1 + V_2}$ $\quad pH = -\log C_1'$

$HX_1 + H_2O \longrightarrow X_1^- + H_3O^+$

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

$C_1' = \frac{C_1 V_1}{V_1 + V_2}$

$C_2' = \frac{C_2 V_2}{V_1 + V_2}$

$V_T = V_1 + V_2$

$[H_3O^+]$ $[OH^-]$ $[X_1^-]$ $[HX_1]$ $[X_2^-]$

ENS : $[H_3O^+] = [X_1^-] + [A^-] +$ ~~$[OH^-]$~~

C.M$_1$: $C_1' =$ ~~$[HX_1]$~~ $+ [X_1^-]$

C.M$_2$: $C_2' = [HA] + [A^-]$

$K_A = \frac{[A^-][H_3O^+]}{[HA]} = \frac{[A^-][H_3O^+]}{C_2' - [A^-]}$

$K_A = \frac{([H_3O^+] - [X_1^-])[H_3O^+]}{C_2' - [A^-]}$ (with $[X_1^-] = C_1'$)

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$$K_A = \frac{[H_3O^+]^2 - C_2'[H_3O^+]}{C_2' + C_1' + [H_3O^+]}$$ Eq 2ème degré

$$[H_3O^+]^2 - C_1'[H_3O^+] - K_A(C_2' - C_1') + K_A[H_3O^+]$$

$$[H_3O^+]^2 + (K_A - C_1')[H_3O^+] - K_A(C_2' - C_1') = 0$$

$$\Delta = b^2 - 4ac = (K_A - C_1')^2 + 4K_A(C_2' + C_1')$$

$$[H_3O^+] = \frac{-(K_A + C_1') + \sqrt{\Delta}}{2}$$

$$pH = -\log\left(\frac{-(K_A + C_1') + \sqrt{\Delta}}{2}\right)$$

$$\Downarrow$$

$$pH = -\log(C_1')$$ pH imposé par l'acide fort

Remarque

Le plus souvent

Si : C_1 et C_2 sont voisins ou : $C_1 > C_2$, la quantité de $[H_3O^+]$ produit par l'ionisation de l'acide faible est negligeable devant celle provenant de l'acide fort. et le volume de $[H_3O^+]$ est très proche de C_1 =>

$$pH = -\log C_1$$