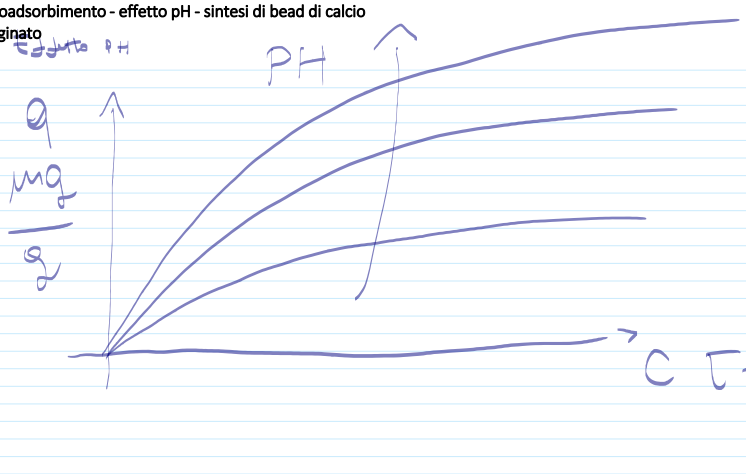
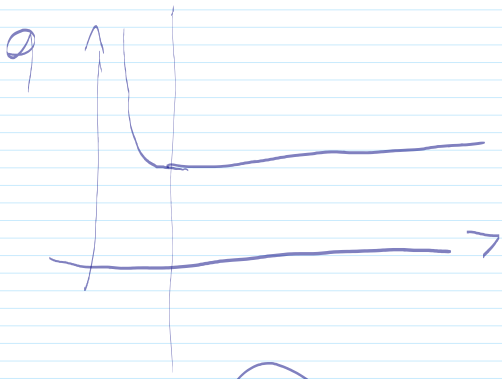
Bioadsorbimento - effetto pH - sintesi di bead di calcio alginato



$$S_1H \rightleftharpoons S_1^- + H^+$$

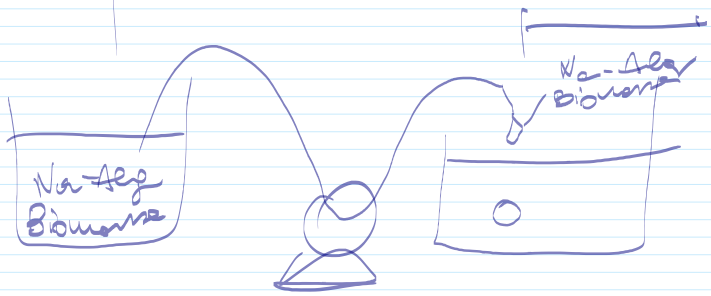
$$S_2H \rightleftharpoons S_2^- + H^+$$

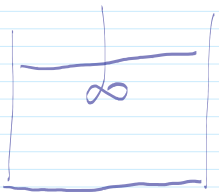
$$S_3H^+ \rightleftharpoons S_3 + H^+$$



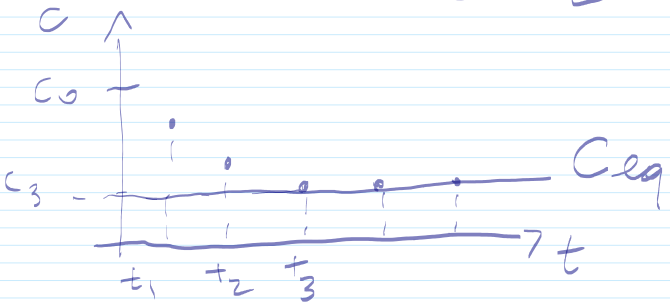
C_M mg/L

$q(C_M)$ mg/g



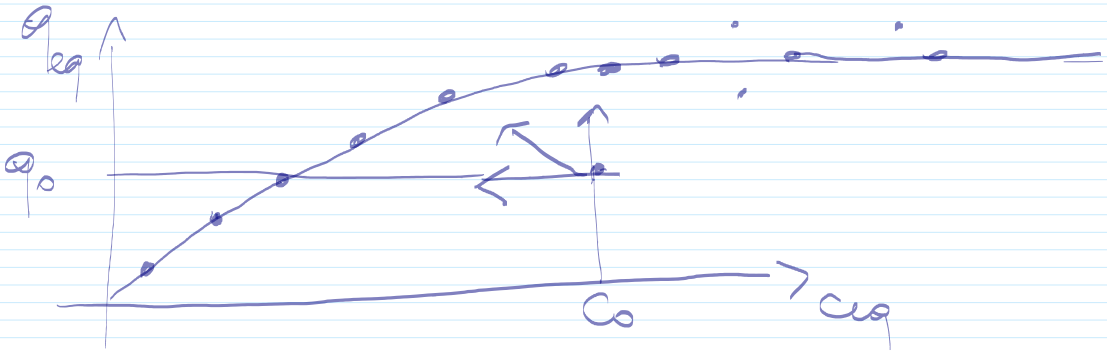


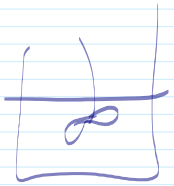
m g di biomassa
V mL di soluzione
C_0 $\frac{mg}{L}$ di metallo in sol



$$q_0 m + C_0 V = q(t) m + C(t) V$$

$$q = \frac{(C_0 - C(t)) V}{m}$$

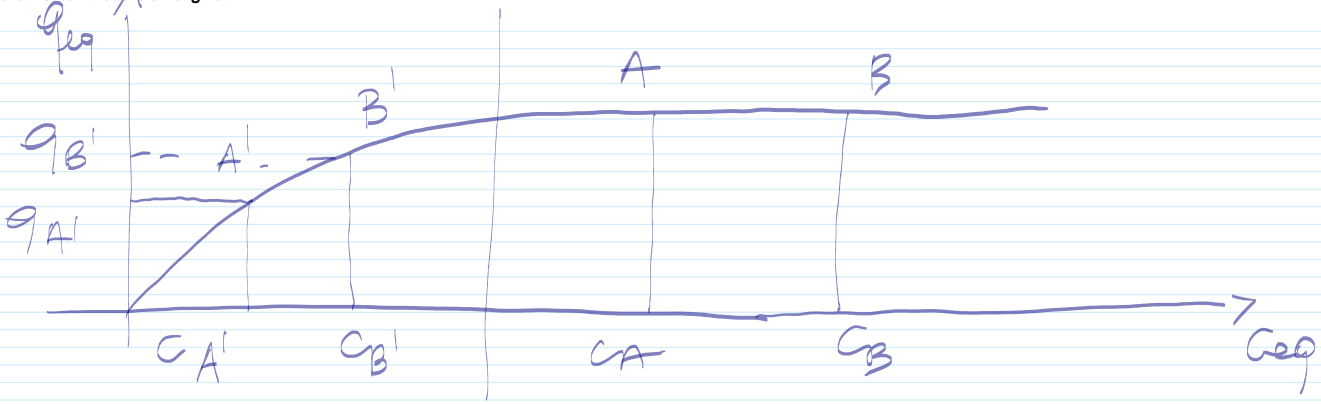


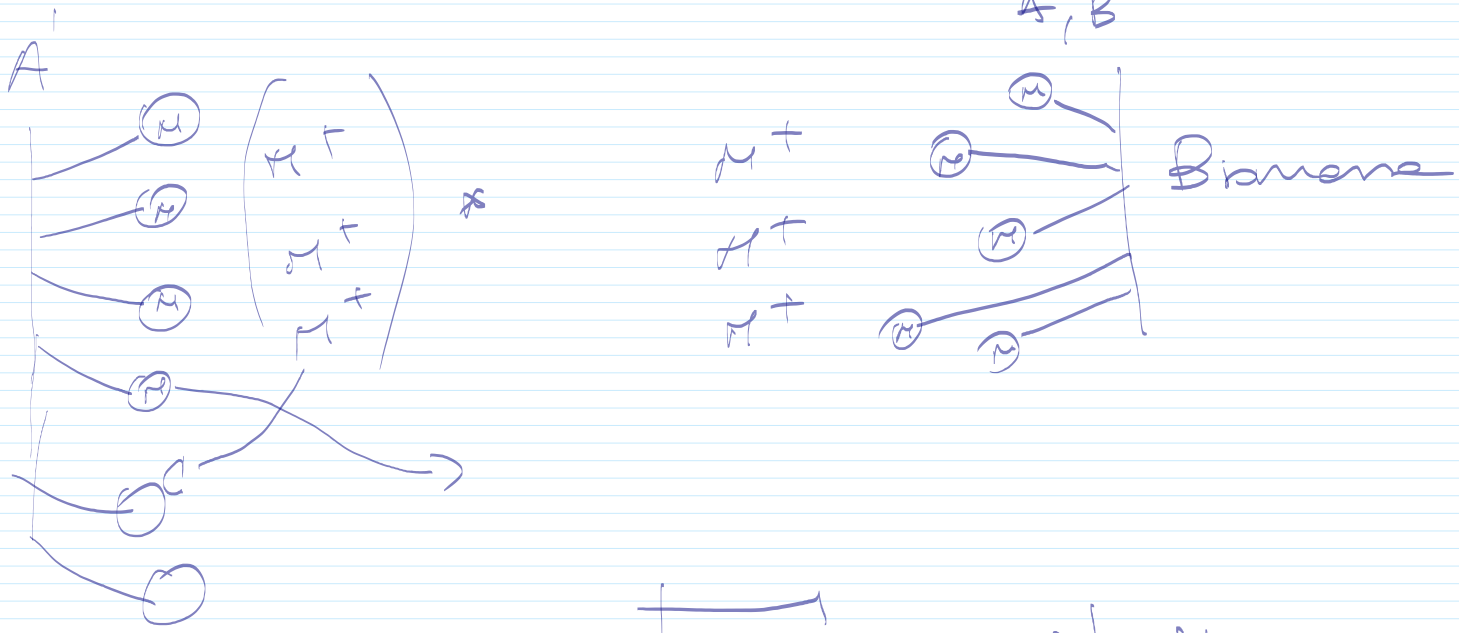


Dati: $q_0, C_0, q_{eq} = f(C_{eq})$

Problemi: q_{eq}, C_{eq}

$$\begin{cases} q_0 m + C_0 V = q_{eq} m + C_{eq} V \\ q_{eq} - f(C_{eq}) = 0 \end{cases}$$





$$\theta = \frac{N \text{ siti occupati}}{N \text{ siti TOT.}}$$

$$r_A = k_A C (1-\theta)$$

$$r_D = k_D \theta$$

$$r_A = r_D \iff k_A C (1-\theta) = k_D \theta$$

$$k_A C - k_A C \theta = k_D \theta \Rightarrow \theta = \frac{k_A C}{k_A C + k_D} =$$

$$= \left[\frac{(k_A/k_D) C}{(k_A/k_D) C + 1} \right] = \frac{bC}{bC+1} \; ; \; b = \frac{k_A}{k_D}$$

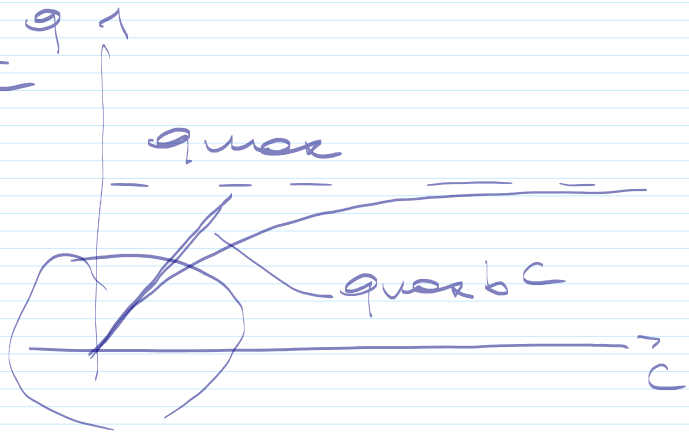
$$\theta = \frac{bC}{bC+1} \qquad b = \frac{k_A}{k_D}$$

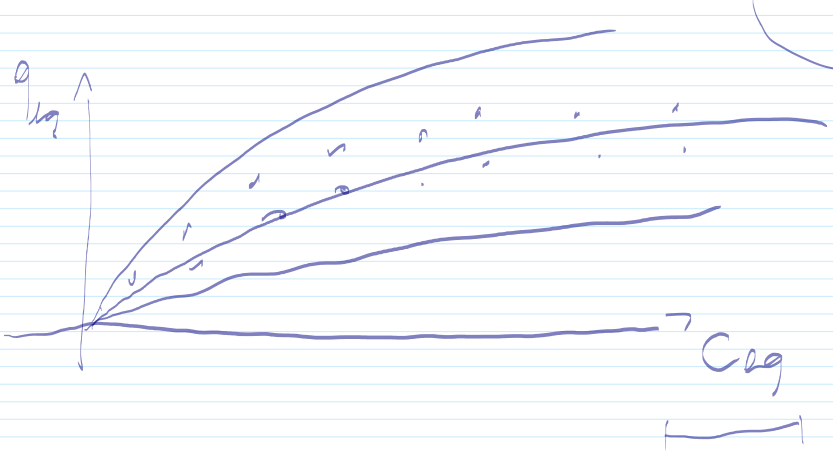
$$\theta = \frac{(N \text{ siti occupati}/N_{AV}) \cdot P_{M^{n+}}/M/1000}{(N \text{ siti TOT}/N_{AV}) \cdot P_{M^{n+}}/M/1000} = \frac{q}{q_{max}}$$

$$\frac{q}{q_{max}} = \frac{bC}{bC+1} \Rightarrow q = \frac{q_{max}\, bC}{bC+1}$$

$bC \ll 1 \qquad q \simeq q_{max}\, bC$

$bC \gg 1 \qquad q \simeq q_{max}$

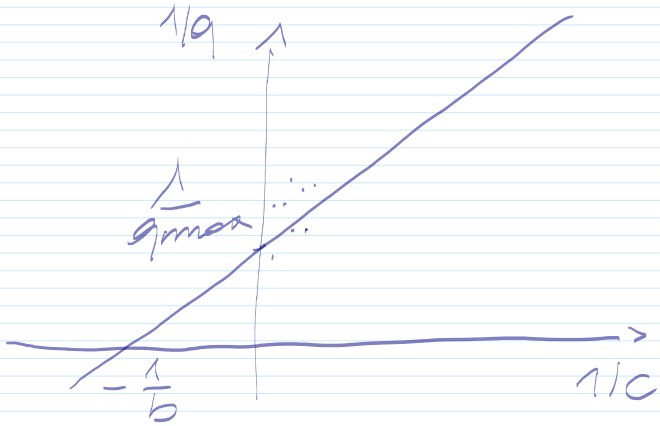




$$q = \frac{q_{max}\, bC}{bC+1}$$

$$\frac{1}{q} \simeq \frac{1}{q_{max} b} \cdot \frac{1}{C} + \frac{1}{q_{max}}$$

$$y = a\,x + b$$



Estensione modello di Langmuir per sistemi multicomponente

$$q = \frac{q_{max}\, bc}{bc+1}$$ singola componente

$$q_i = f_i(c_1 \dots c_N)$$

2-comp.

$$q_1 = f_1(c_1, c_2) \qquad q_2 = f_2(c_1, c_2)$$

$$q_1 = f_1(c_1) \qquad q_2 = f_2(c_2)$$

$$q_1 = \frac{q_{max,1}\, b_1 c_1}{1 + b_1 c_1 + b_2 c_2} \; ; \quad q_2 = \frac{q_{max,2}\, b_2 c_2}{1 + b_2 c_2 + b_1 c_1} \quad (**)(A)$$

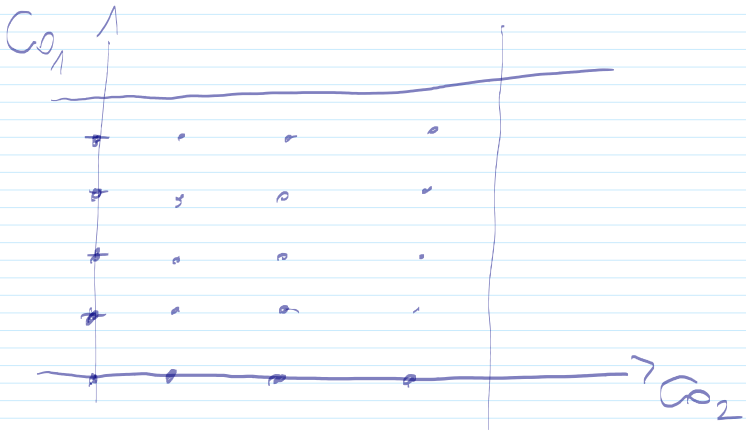
più in generale per N inutili

$$q_i = \frac{q_{max,i}\, b_i c_i}{1 + \sum_j b_j c_j} \quad (*)$$

$$q_1 = \frac{q_{max}\, b_1 c_1}{1 + b_1 c_1 + b_2 c_2} \; ; \quad q_2 = \frac{q_{max}\, b_2 c_2}{1 + b_1 c_1 + b_2 c_2} \quad (B)$$

$$q_1 = \frac{q_{max,1}\, b_1 c_1 / n_1}{1 + \frac{b_1 c_1}{n_1} + \frac{b_2 c_2}{n_2}} \; ; \quad q_2 = \frac{q_{max,2}\, b_2 c_2 / n_2}{1 + b_1 \frac{c_1}{n_1} + b_2 \frac{c_2}{n_2}} \quad (C)$$

$$q_1 = \frac{q_{max,1}\, b_1 c_1}{1 + b_1 c_1 + b_2 c_2} \quad ; \quad q_2 = \frac{q_{max,2}\, b_2 c_2}{1 + b_1 c_1 + b_2 c_2}$$



singolo metallo
N esperimenti

2 metalli
$N \cdot N = N^2$

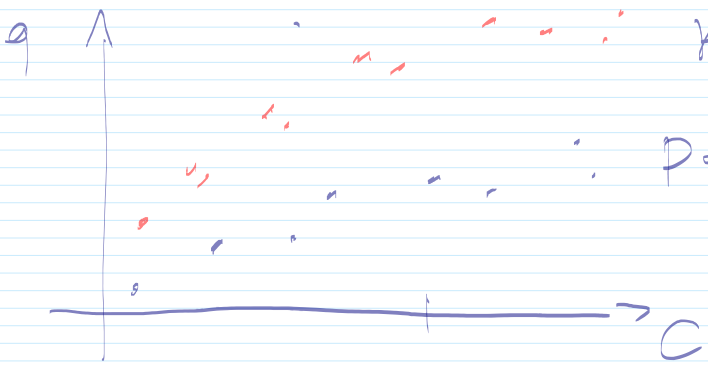
Se non ho interazione

q_{max_1}, b_1 ⟶ N esperimenti con solo M_1

q_{max_2}, b_2 ⟶ N esperimenti con solo M_2

$2N$

N	2	3	4	5
con interazione N^2	4	9	16	25
senza INT. $2N$	4	6	8	10



$SH = S^- + H^+$

$$q = \frac{q_{max} \, bC}{bC + 1}$$

$S^- + H^+ = SH$

$$K_H = \frac{[SH]}{[S^-][H^+]}$$

$S^- + M^+ = SM$

$$K_M = \frac{[SM]}{[S^-][M^+]} \quad (*)$$

$$[S_{TOT}] = [S^-] + [SH] + [SM] = \left(\frac{[SM]}{K_M [M^+]}\right) + K_H [S^-][H^+] + [SM] =$$

$$= \frac{[SM]}{K_M [M^+]} + K_H \frac{[SM]}{K_M [M^+]} \cdot [H^+] + [SM] =$$

$$= [SM] \left(\frac{1}{K_M [M^+]} + \frac{K_H}{K_M} \cdot \frac{[H^+]}{[M^+]} + 1 \right)$$

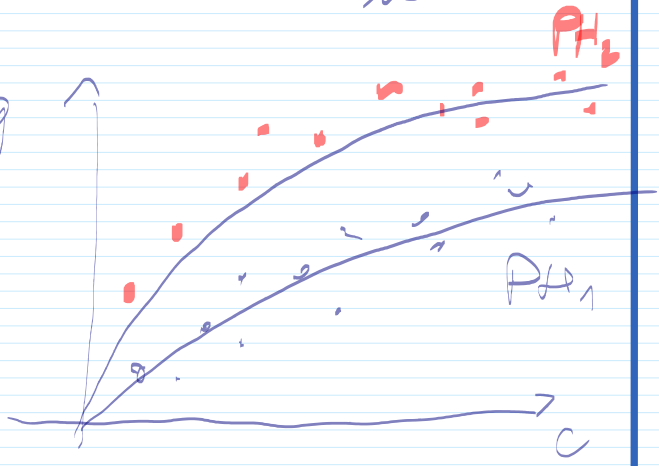
$$[SM] = \frac{[S_{TOT}]}{\frac{1}{K_M [M^+]} + \frac{K_H}{K_M} \frac{[H^+]}{[M^+]} + 1} = \frac{[S_{TOT}] K_M [M^+]}{1 + K_H [H^+] + K_M [M^+]}$$

$$[SM] = \frac{[S_{TOT}]\, k_M [M^+]}{1 + k_H [H^+] + k_M [M^+]}$$

$$pH = -\log_{10} [H^+]$$

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

$$q = \frac{q_{max}\, b\, C}{1 + k_H 10^{-pH} + b\, C}$$



parametri:
q_{max}, b, k_H

Esercizio 1

$$S_1^- + H^+ = S_1 H \qquad S_2^- + H^+ = S_2 H$$

$$S_1^- + M^+ = S_1 M \qquad S_2^- + M^+ = S_2 M$$

$q = f([M^+]) = f(C)$

$[S_{1TOT}]$, k_{M1}, k_{H1}
$[S_{2TOT}]$, k_{M2}, k_{H2}

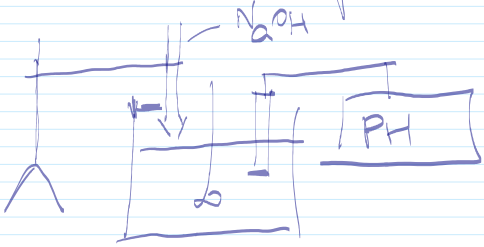
Esercizio 2

$$S_1^- + H^+ = S_1 H \qquad S_2 + M^+ = S_2 M^+$$

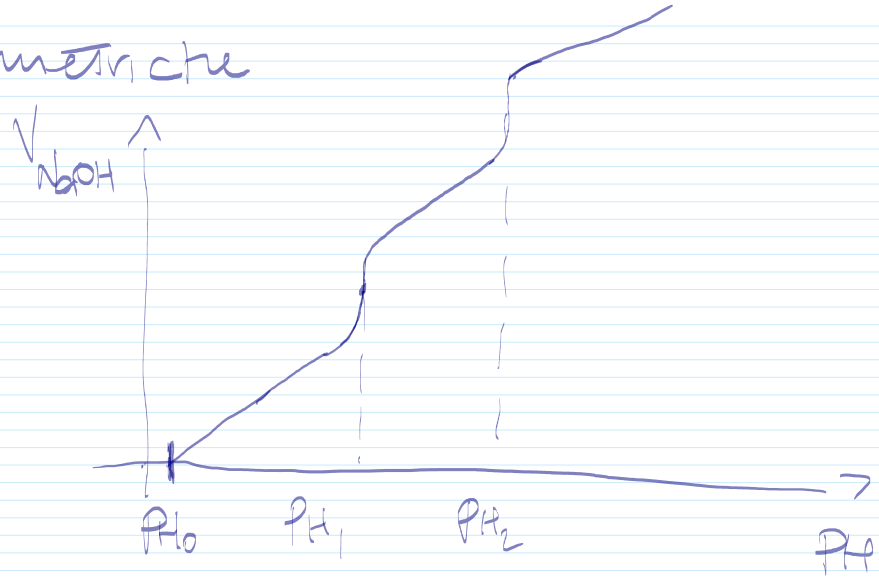
$$S_1^- + M^+ = S_1 M$$

$q = f(C)$ $\quad C = [M^+]$

Titolazioni potenziometriche



V_{HCl}



$$S_1H \rightleftharpoons S_1^- + H^+ \quad (A)$$

$$S_1H^+ \rightleftharpoons S_1 + H^+$$

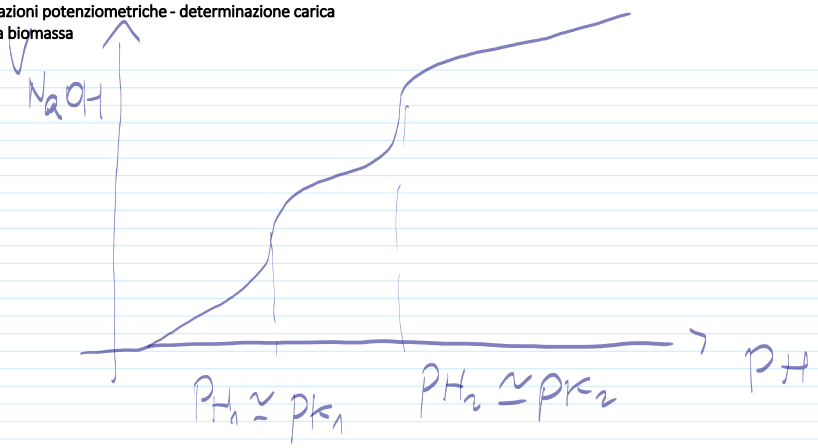
$$K_{H_1} = \frac{[S_1H]}{[S_1^-][H^+]}$$

$$[S_1H] \simeq [S_1^-]$$

$$K_{H_1} \simeq \frac{1}{[H^+]} = [H^+]^{-1}$$

$$\log K_{H_1} \simeq -\log [H^+]$$

$$pK_1 = \log K_{H_1} \simeq pH_1$$



V_{HCl}, $[HCl]$

V_{NaCl}, $[NaCl]$

V_{NaOH}, $[NaOH]$

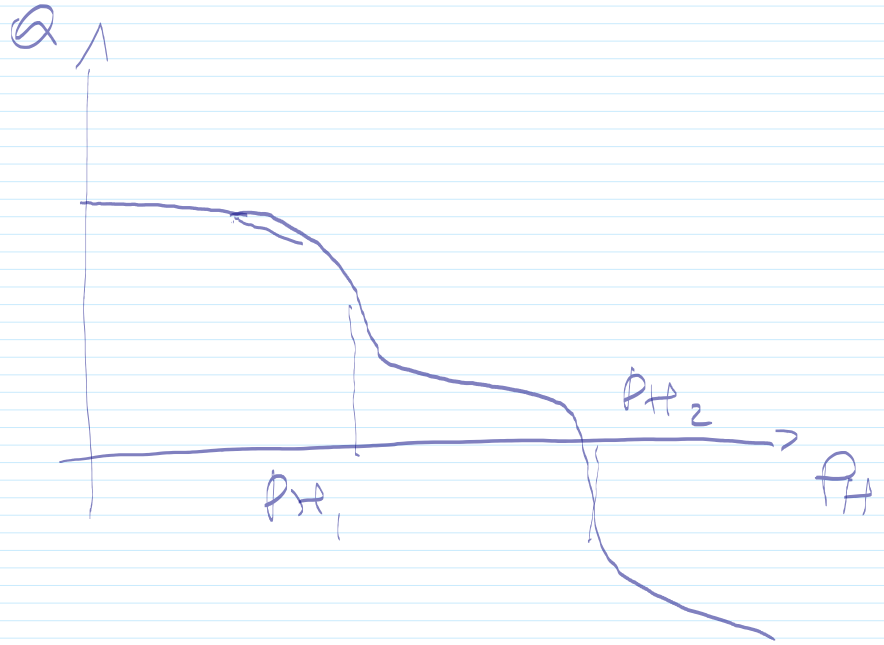
$Q = f(pH)$

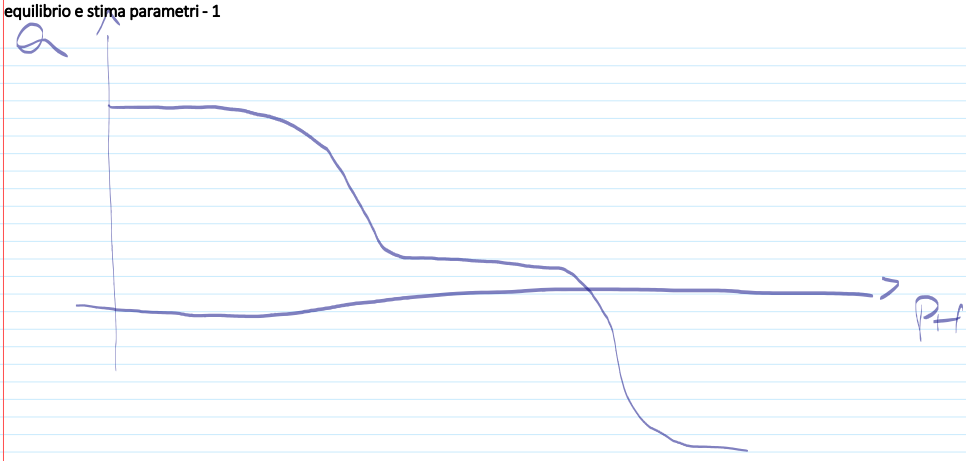
$Q[=] \frac{moli}{g}$ $\quad m[=] g_{ss}$

$$n_{Na^+} + n_{H^+} = n_{OH^-} + n_{Cl^-} + Q_m$$

$$V_{NaCl} \cdot [NaCl] + (V_{NaOH} \cdot [NaOH]) + V_{TOT} \cdot 10^{-pH} = V_{TOT} 10^{-(14-pH)} + V_{NaCl} \cdot [NaCl] + V_{HCl} \cdot [HCl] + (Q \cdot m)$$

V_{NaOH}	pH	Q
V_{NaOH_1}	pH_1	Q_1
V_{NaOH_2}	pH_2	Q_2
V_{NaOH_3}	pH_3	Q_3
⋮		
V_{NaOH_N}	pH_N	Q_N





p_H	Q
p_{H_1}	Q_1
⋮	⋮

$$S_1^- + H^+ = [S_1H]$$

$$S_2 + H^+ = [S_2H^+]$$

$$Q_1 = +[S_1^-] - [S_2H^+]$$

$$K_{H_1} = \frac{[S_1H]}{[S_1^-]\,[H^+]} \quad (A) \;;\qquad K_{H_2} = \frac{[S_2H^+]}{[S_2]\,[H^+]}$$

$$[S_{1TOT}] = [S_1^-] + [S_1H] = [S_1^-] + K_{H_1}\cdot[S_1^-]\cdot[H^+] =$$

$$= [S_1^-]\cdot(1 + K_{H_1}\cdot[H^+])$$

$$[S_1^-] = \frac{[S_{1TOT}]}{1 + K_{H_1}[H^+]} \;;$$

$S_1^- + H^+ = S_1H$

$K_{H_1} = \frac{[S_1H]}{[S_1^-][H^+]}$

~~$S_2 + H^+ = S_2H$~~

$S_2^- + H^+ = S_2H$

$K_{H_2} = \frac{[S_2H^+]}{[S_2][H^+]}$ *

$[S_{2TOT}] = [S_2] + [S_2H^+] =$

$= \frac{[S_2H^+]}{K_{H_2} \cdot [H^+]} + [S_2H^+] = [S_2H^+] \cdot \left(\frac{1}{K_{H_2}[H^+]} + 1 \right)$

$[S_2H^+] = \frac{[S_{2TOT}]}{\frac{1}{K_{H_2}[H^+]} + 1} = \frac{[S_{2TOT}] K_{H_2}[H^+]}{1 + K_{H_2}[H^+]}$

$Q = [S_1^-] - [S_2H^+] = \frac{[S_{1TOT}]}{1 + K_{H_1} 10^{-PH}} - \frac{[S_{2TOT}] K_{H_2}}{1 + K_{H_2} 10^{-PH}}$

$Q = f(PH)$

parametri:

$[S_{1TOT}]$, $[S_{2TOT}]$, K_{H_1}, K_{H_2}