Properties of cation exchange :

1-Reversibility : cation exchange reaction are (CER)reversible reaction Or near it, but there are some exceptions such as:

A-Poly valent cations except (Fe) or trace elements.

B- Some cations.

C-Adsorption of some large organic molecules such as pesticides.

2- Stoichiometry :

$CaX + 2NH_4^+$ Soluble $= 2NH_4X$ + Soluble Ca

But some times there are hysterias phenomenon.

3-Speed: Exchange reactions are rapid.

4-Mass action: Due to their reversibility the CER can be driven in either forward or reverse direction by multipilatry the concentration of reactants or and products for example:

CaX + 2Na (high concentration) = Na2 X + Ca(low concertation)

$CaX + Na_2CO_3 = Na_2X + CaCO_3\downarrow$ (precipitation).

$NH_4^+X + NaOH = NaX + NH_4OH = NaX + H_20 + NH_3\uparrow$

5- Valence dilution effect : For example

$$\frac{(NH_4)_2\,X}{CaX} = K\,\frac{(NH_4)^2}{(Ca)}$$

If concentration of NH_4^+ =1 mmole /L and Ca^{2+} = 1 mmole /L

The ratio = $\frac{1}{1}$ =1

But if the solution diluted 10 times the ratio will change to

$$The\ ratio = \frac{(NH_4^+)^2}{Ca^{2+}} = \frac{(0.1)^2}{0.1} = 0.1$$

What is the application of this law in water classification?

6-Complementary cations:

a: Ca-Al + NH_4^+ = Replace is easier.

b: Ca-Na + NH_4^+

Why replacing of Ca by NH_4 in a is easier than b?

7- Anion effect: The anion associated with replacing cation can affect by cation exchange (CE) depending on types of anions and products for example:

A- More weakly dissociated :

$$HX + Na^{+} + OH^{-} \rightleftharpoons NaX + H_2O$$

$$HX + Na^{+} + Cl^{-} \rightleftharpoons NaX + H^{+} + Cl^{-}$$

Why the behavior of the second reaction is differing from the first one as shown by red arrow? Explain it.

B- Less soluble:

$$AlX + 3Na + 3OH \rightleftharpoons 3NaX + Al(OH)_3 \downarrow$$

$$AlX + 3Na + 3Cl^{-} \rightleftharpoons 3NaX + Al^{3+} + 3Cl^{-}$$

C –More volatile and non volatile :

$$2HX + CaCO_3 \rightleftharpoons CaX + H_2CO_3 \rightleftharpoons CaX + H_2O + CO_2\uparrow$$

$$2HX + CaSO_4 \rightleftharpoons CaX + H_2SO_4$$ (Non volatile)

Langmuir equation or model :

- Suppose that the covered soil surface at any time = Θ and non covered portion = $1- \Theta$ depending on above :
- Rate of adsorption $\propto c(1- \Theta)$
- Rate of adsorption = $K_1 C_1 (1- \Theta)$
- C = concentration of equilibrium
- Rate of desorption $\propto \Theta$
- Rate of desorption = $K_2 \Theta$

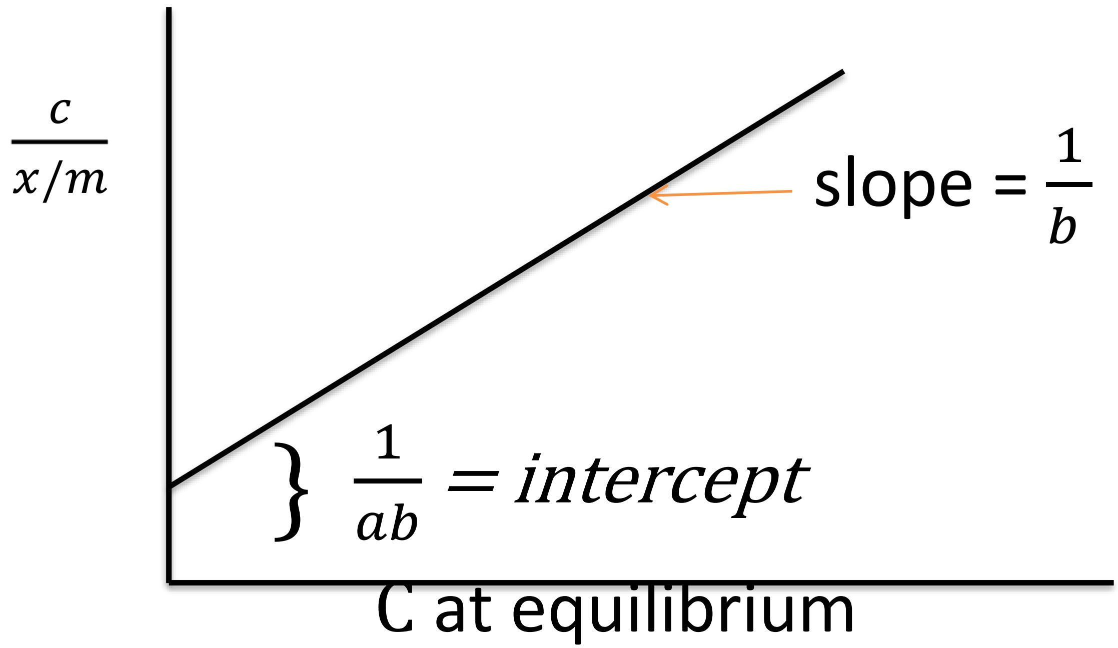
- At equilibrium point :
- Rate of adsorption = rate of desorption
- $\therefore K_1 C (1- \Theta) = K_2 \Theta$
- $\therefore K_1 C = K_2 \Theta + K_1 C \Theta$
- $\therefore K_1 C = \Theta (K_2 + K_1 C)$
- $\Theta = \frac{K_1 C}{K_2 + K_1 C}$
- If $\frac{K_1}{K_2} = K$ or $= a$
- $\frac{1}{\Theta} = \frac{K_2 + K_1 C}{K_1 C}$

- $\frac{1}{\Theta} = \frac{K_2}{K_1\ C} + \frac{1}{\Theta} = \frac{K_1\ C}{K_1\ C}$
- $\frac{1}{\Theta} = 1 + \frac{K_2}{K_1\ C}$
- $\frac{1}{\Theta} = 1 + \frac{1}{a\ C}$ (because $\frac{K_1}{K_2} = K$ or = a
- $\frac{1}{\Theta} = \frac{ac+1}{a\ c}$
- $\frac{x}{m} \propto \Theta$ ……

$\therefore \frac{x}{m} = b\ \Theta$ b=k and $\Theta = \frac{ac}{a\ c+1}$

$\therefore$ [$\frac{x}{m} = \frac{abc}{a\ c+1}$] Dividing both sides by c .

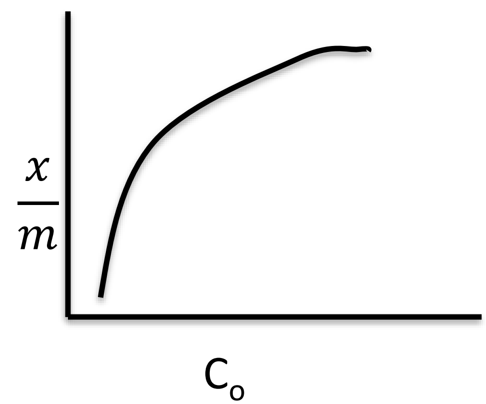
- $\frac{x/m}{c} = \frac{\text{ac}}{\text{a } c+1}$
- $\therefore \frac{c}{x/m} = \frac{1+ac}{ab}$
- $\therefore \frac{c}{x/m} = \frac{1}{ab} + \frac{c}{b}$
- c/x/m = $\frac{1}{ab} + \frac{1}{b}$ C



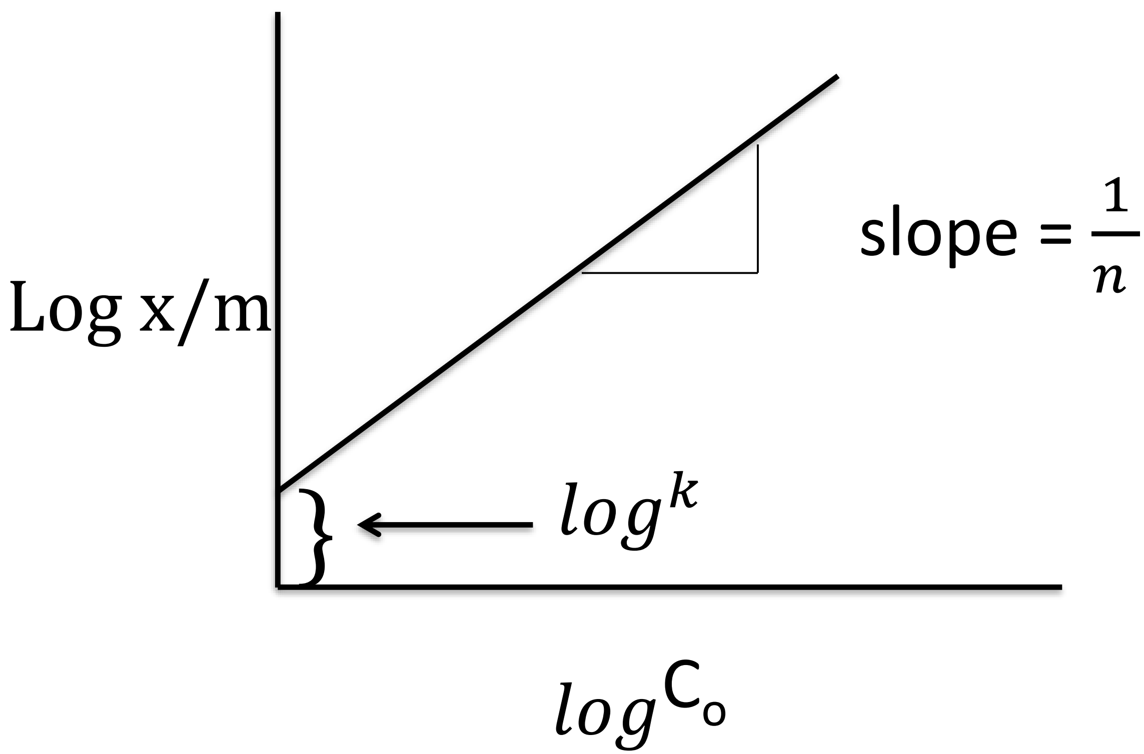
- A=K= affinity constant
- B=maximum adsorption
- $\frac{slope}{intercept} = \frac{\frac{1}{b}}{\frac{1}{ab}}$
- $= \frac{1}{b} * \frac{ab}{1} =$ a or K

Freandlich equation:

- It used successfully gas adsorption and it can be use in adsorption of Mo and boron.
- $\frac{x}{m} = KC.^{\frac{1}{n}}$
- $\frac{x}{m} =$
- K= Empirical constant
- C_o = concentration at equilibrium
- N= Empirical constant



- But logarithmic form in as follow
- Log $\frac{x}{m}$ = log^{k}+ $\frac{1}{n}$ log^{C_o}



Gapon model :

- $Ca_{\frac{1}{2}}X_{(soil\ surface)} + Na \rightleftharpoons \frac{1}{2}Ca + NaX$
- $KG = \frac{[Ca]^{1/2}[NaX]}{[Na][Ca_{\frac{1}{2}}X]}$
- $KG = \frac{[NaX]}{[CaX]} \cdot \frac{[\sqrt{Ca}]}{[Na]}$
- $\therefore \frac{NaX}{CaX} = KG \,/\, \frac{\sqrt{Ca}}{Na}$ in mmol/L
- $\frac{NaX}{CaX} = KG * \frac{Na}{\sqrt{Ca}}$
- Depending on activity: meq/100g soil
- $\frac{NaX}{CaX} = KG \frac{Na*\gamma Na}{\sqrt{Ca*\gamma Ca}}$

- While $\frac{\gamma Na}{\sqrt{\gamma Ca}}$ = constant
- $\therefore \frac{NaX}{CaX}$= KG $\frac{Na}{\sqrt{Ca}}$ (depending on activity)
- ESR = KG SAR
- After that Mg was added to the Gapon model as follow
- $\frac{NaX}{CaX+MgX}$ = KG $\frac{Na}{\sqrt{Ca+Mg}}$ ← mmol/L

↑

- Meq/100g soil

↓

- $\frac{NaX}{CaX+MgX}$ = KG $\frac{Na}{\sqrt{\frac{Ca+Mg}{2}}}$ ← meq/L

- What are the benefit of KG value?? What are the modifications??
- <u>Important Not :</u>
- In Gapon equation CEC = Ca_x + Mg_x + Na_x
- Na_x = Na adsorption
- Ca_x = Ca adsorption
- CEC = Na ad + Ca ad (1923)
- CEC = Na ad + Ca ad + Mg ad (1980)
- $\frac{NaX}{CaX}$ = KG $\frac{Na}{\sqrt{Ca}}$
- $\frac{NaX}{CaX}$ = ESR exchangeable sodium ratio
- Or ESR = $\frac{NaX}{CaX+MgX}$
- $\frac{NaX}{CEC} * 100 = \mathrm{ESP}$ Echangable Na %

- For example : calculate KG if you are given the following information :
- 1- Na x = 10 meq/100g soil
- CEC= 20 meq/100g soil
- Soluble Na = 8 mmole/L
- Soluble Ca = 9 mmole/L
- $\frac{NaX}{CaX}$= KG $\frac{Na}{\sqrt{Ca}}$
- $\frac{NaX}{CEC-NaX}$= KG $\frac{Na}{\sqrt{Ca}}$
- $\frac{10}{20-10}$= KG $\frac{8}{\sqrt{9}}$ ⟹ 10/10=KG*8/3
- 1= KG*8/3 ⟹ 3=KG*8
- KG= 3/8