

Aspects cinétique de la R^o d'oxydo-réduction

* $\text{dox} + m\bar{e} \rightarrow \text{Red}$: Réduction $\rightarrow$ cathode (+)

$$v_{\text{Red}} = -\frac{1}{\alpha} \frac{d[\text{dox}]}{dt} = \frac{1}{\beta} \frac{d[\text{Red}]}{dt}$$

* $\text{Red} \rightarrow \text{dox} + m\bar{e}$: oxydation $\rightarrow$ anode (-)

$$v_{\text{ox}} = -\frac{1}{\beta} \frac{d[\text{Red}]}{dt} = \frac{1}{\alpha} \frac{d[\text{dox}]}{dt}$$

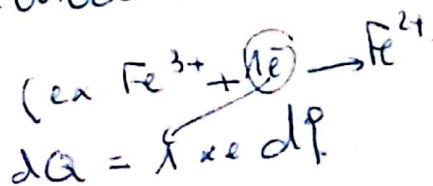
impose v - avancement de la R^o

$$v = \frac{d\xi}{dt}$$

on note dQ : d'écoulement de charge électrique

échangée traversant l'interface d'électrode et la solution.

$$dQ = m e d\xi \text{ pour 1 atome.}$$



$$dQ = n F d\xi \text{ pour 1 mole.}$$

$$I = \frac{dQ}{dt}$$

$$I = n F v$$

$$\left\{ \begin{array}{l} \text{oxydation } v_{\text{ox}} = n F v_{\text{ox}} \\ \text{Réduction } v_{\text{Red}} = n F v_{\text{Red}} \end{array} \right.$$

vitesse global. $v = v_{\text{ox}} - v_{\text{Red}}$

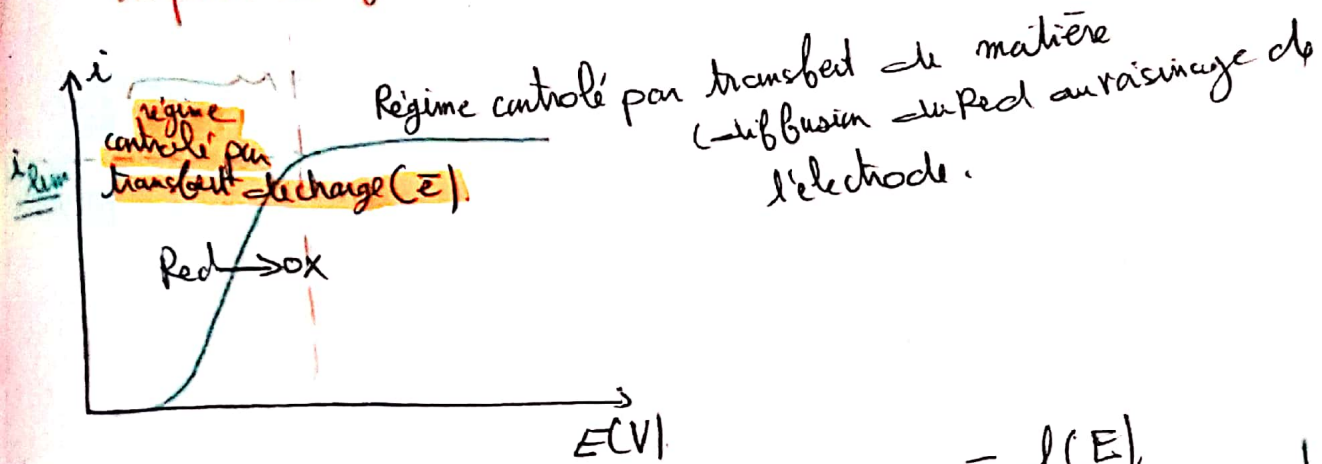
Facteurs cinétiques

* T, C_i : concentration des espèces, S : aire de l'interface
 électrode - solution

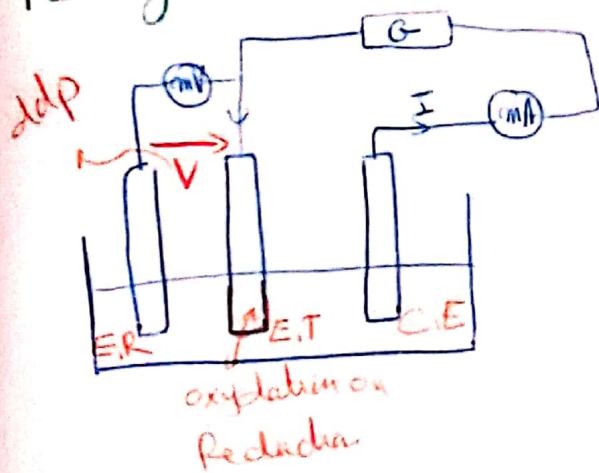


- Nature de l'électrode.
- $\Delta \phi$: V entre l'électrode et la solution.
- si T, S, C_i sont bloqués, on obtient $I = f(E)$.

on peut définir la vitesse surfacique $j = \frac{I}{S}$
 courbe intensité potentiel



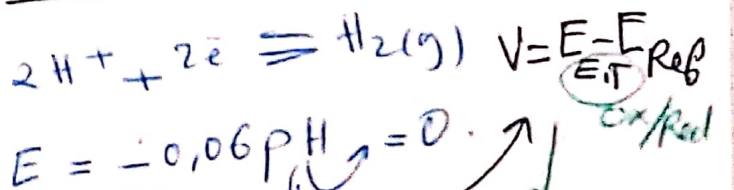
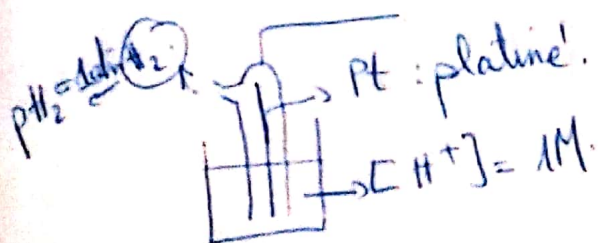
Montage à 3 électrodes $\Rightarrow$ pour mesurer $I = f(E)$



E.T: électrode de travail
 peut jouer le rôle d'une anode ou d'une cathode. Selon la réduction ou oxydation.
 C.E contre électrode (formée par un métal Inerte qui permet la fermeture du circuit.

E.R: électrode de référence

① E.N.H: électrode normale à hydrogène $[H^+] = 1M$
 $P_{H_2} = 1 atm$



$E_{E.N.H} = 0 V$

$V = E_{ox/red}$

$\Delta \phi = \frac{E_{E.T} - E_{ox/red}}{z}$

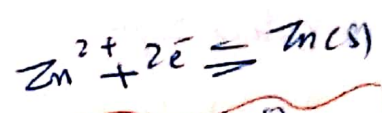
Electrode de zinc calomel saturée

$$E_{C.S} = +0,25V$$

$$V = E_{ox/red} - E_{Ref}$$

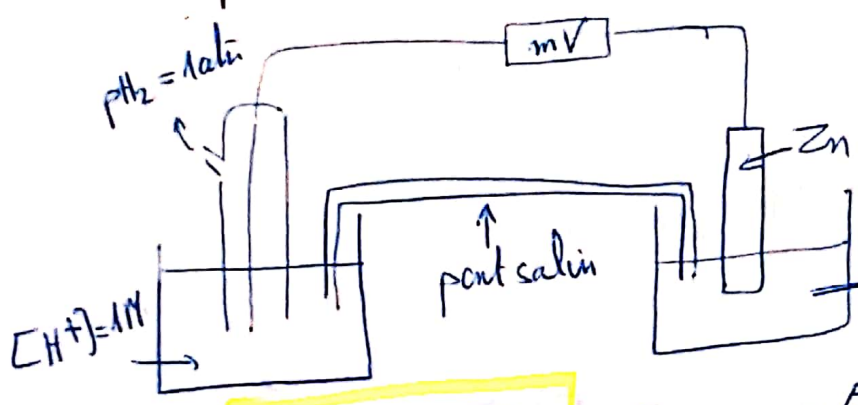
$$V = E_{ox/red} + 0,25V$$

Rq comment peut-on mesurer le potentiel standard du couple $Zn^{2+}/Zn(s)$



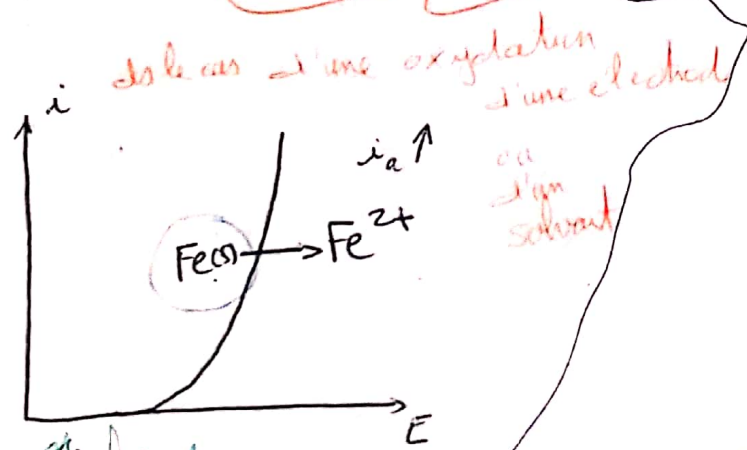
$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0$$

$$[Zn^{2+}] = 1M$$

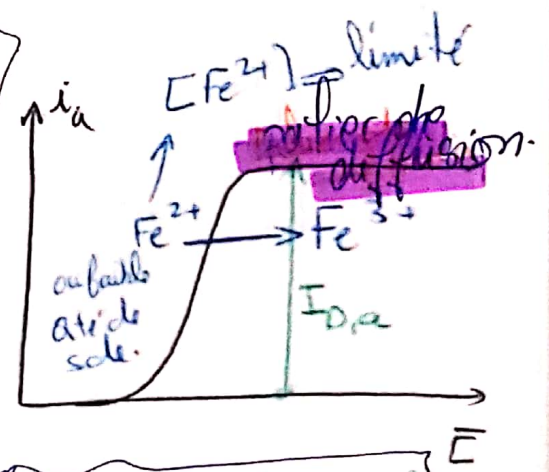


$$f.e.m = E_D - E_R = E_{Zn^{2+}/Zn} - E_{H^+/H_2} = 0$$

$$f.e.m = E_{Zn^{2+}/Zn}^0$$

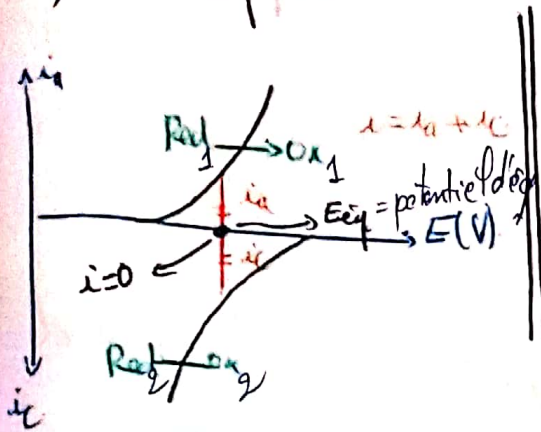


g. electrode solvant
Come H₂O

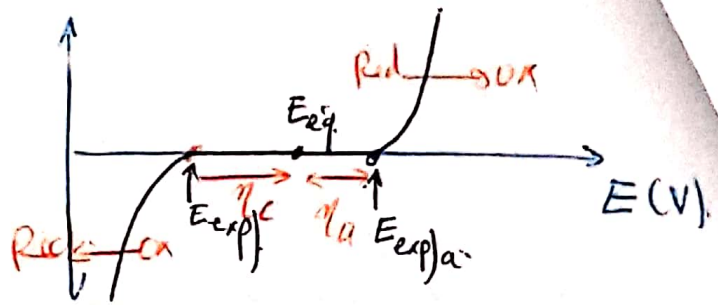


$$I_{D.a} = k(Fe^{2+}) [Fe^{2+}]$$

système rapide



système lent.



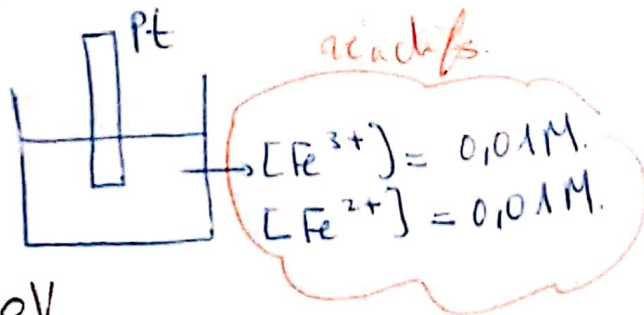
Pour un système rapide, il y a un seul potentiel d'équilibre pour lequel $i = 0$.
 * i_a rapidement dès qu'on s'écarte du potentiel d'équilibre.

Le système ne réagit pas rapidement il faut appliquer une surtension cathodique ou anodique pour démarrer la R^0

$$\eta_a = E_{exp)a} - E_{th} > 0$$

$$\eta_c = E_{exp)c} - E_{th} < 0$$

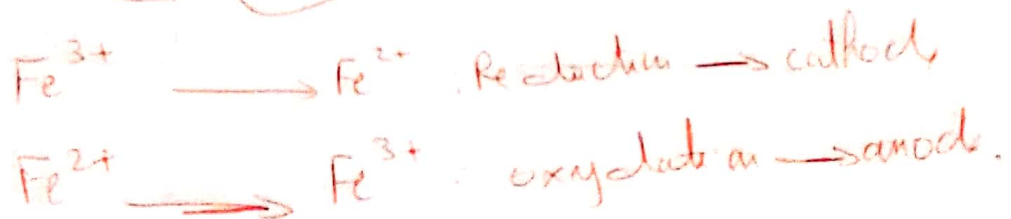
exp 1

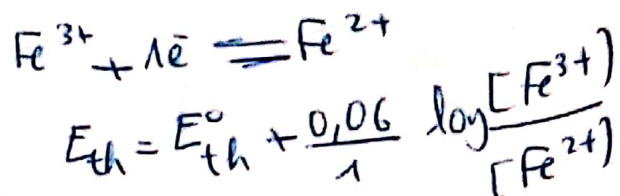
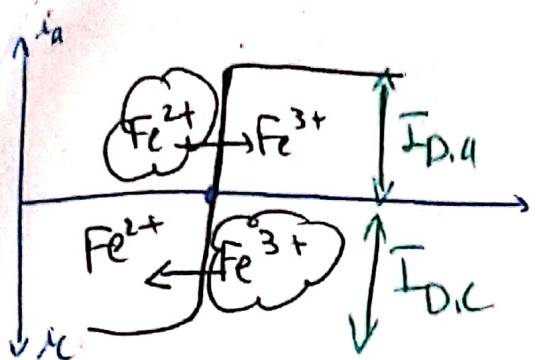


$$E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$$

$$\eta_a = 0V$$

$$\eta_c = 0V$$





$$E_{th} = 0,77 \text{ V}$$

$$\eta_a = E_{exp,a} - E_{th} = 0$$

$$\Rightarrow E_{exp,a} = E_{exp,c} = E_{th}$$

systeme Rapide

$$I_{p,a} = k_p(\text{Fe}^{2+}) [\text{Fe}^{2+}]$$

$$I_{p,c} = k_p(\text{Fe}^{3+}) [\text{Fe}^{3+}]$$

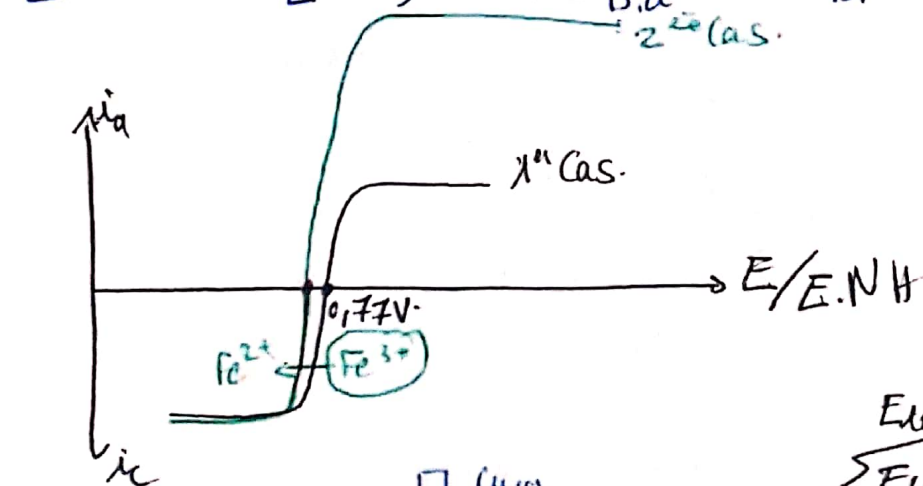
and $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] \rightarrow I_{p,a} = I_{p,c}$

* 2nd Cas: $[\text{Fe}^{3+}]' = 0,1 \text{ M}$
 $[\text{Fe}^{2+}]' = 0,3 \text{ M} \rightarrow E'_{th} = 0,77 + 0,06 \log \frac{0,1}{0,3}$

$$E'_{th} = 0,71 \text{ V}$$

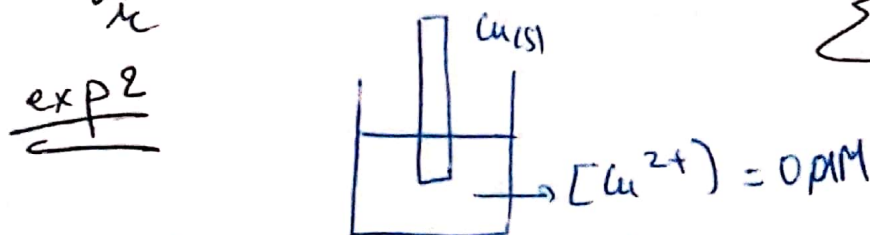
$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]' \Rightarrow I_{p,c} = I'_{p,c}$$

$$[\text{Fe}^{2+}]' = 3 [\text{Fe}^{2+}] \rightarrow I'_{p,a} = 3 I_{p,a}$$

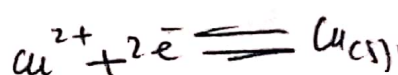
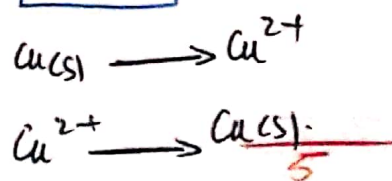


$$E_{th} = E^0 + \frac{0,06}{2} \log 10^{-2}$$

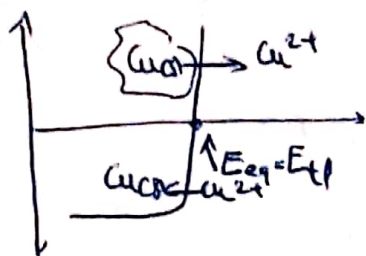
$$E_{th} = 0,28 \text{ V}$$



réactions

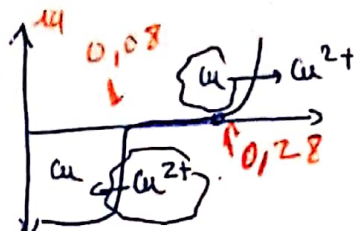


$$\eta_a = \eta_c = 0$$



$$\eta_a = 0$$

$$\eta_c = -0,2V$$



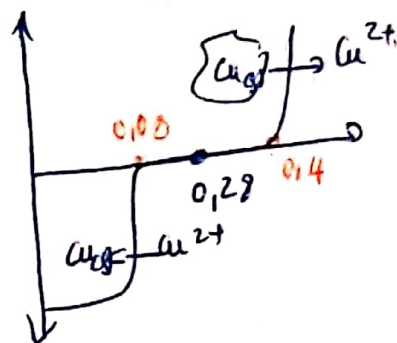
$$\eta_a = 0 \Rightarrow E_{exp,a} = E_{th,a}$$

$$\eta_c = E_{exp,c} - E_{th,c}$$

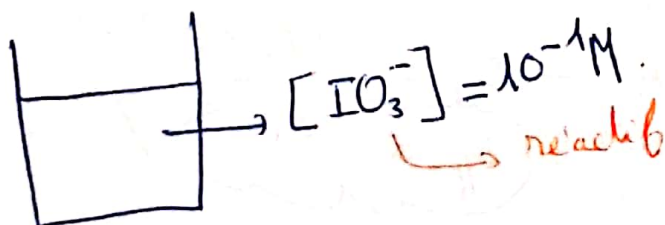
$$\Rightarrow E_{exp,c} = 0,28 - 0,2 = 0,08V$$

$$\eta_a = 0,12V$$

$$\eta_c = -0,2V$$

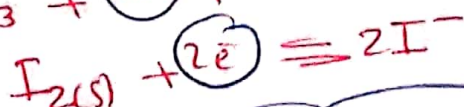
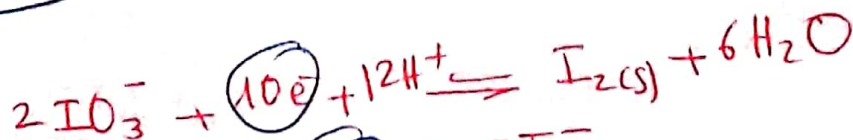
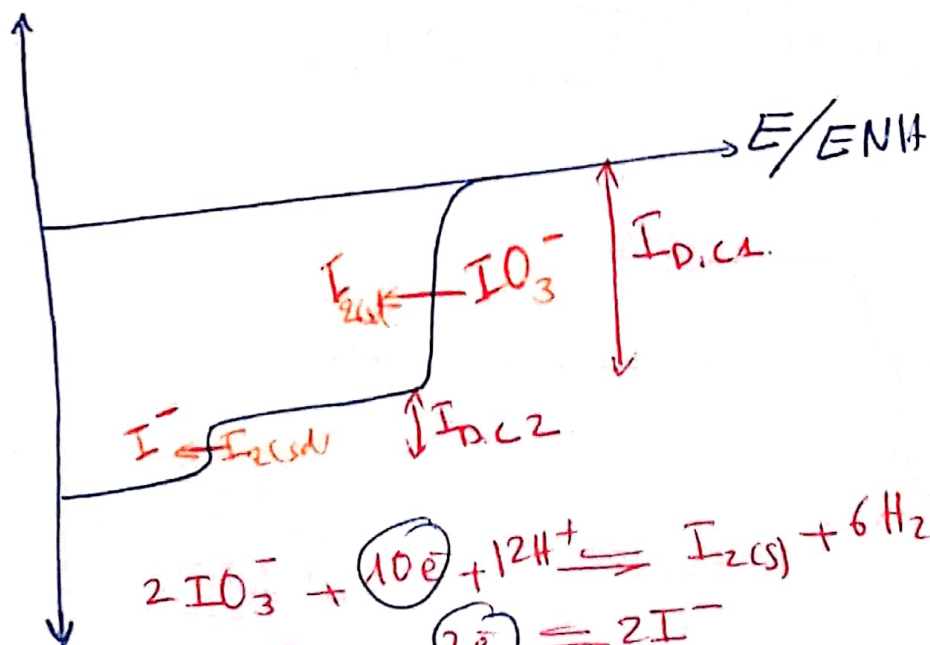


*



$$E^0_{IO_3^- / I_{2csd}} =$$

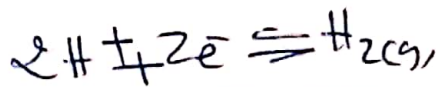
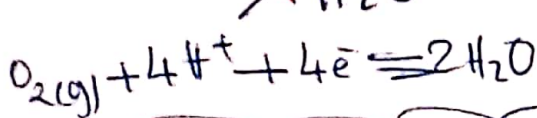
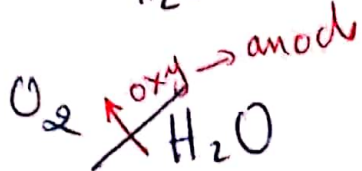
$$E^0_{I_{2csd} / I^-} =$$



$$n\bar{e}_1 = 5 n\bar{e}_2 \Rightarrow I_{D.C.1} = 5 I_{D.C.2}$$

Imitation par le solvant (H_2O).

H_2O est un ampholyte



$E_1 = 1,23 - 0,06 pH (V)$

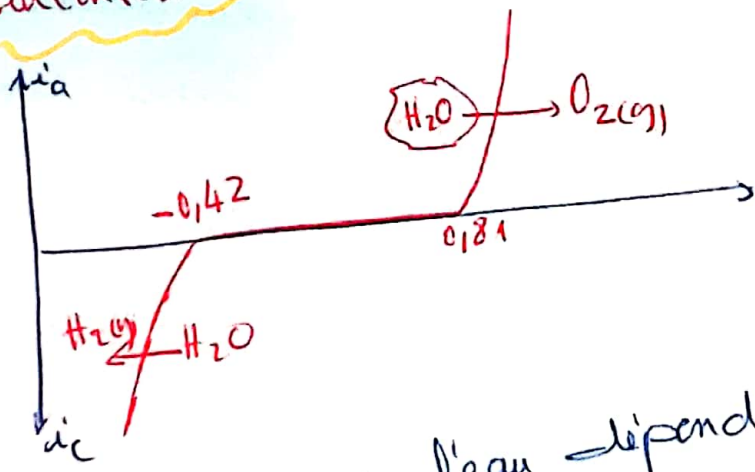
$E_2 = -0,06 pH$

Milieu neutre $\Rightarrow pH = 7$

$E_2 = -0,42V$

$E_1 = 0,81V$

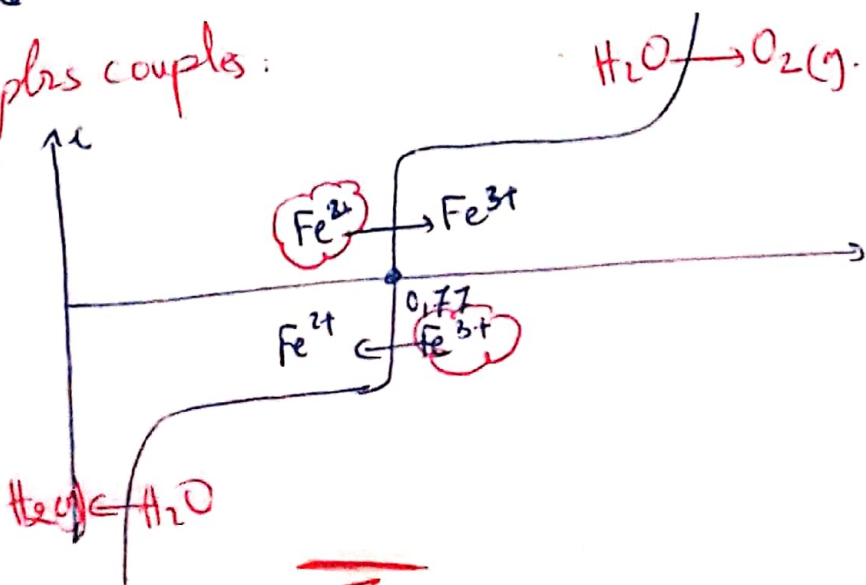
sans surtension.



Rq la réduction de l'eau dépend fortement de la nature du métal utilisé comme électrode.

Présence de pils couples:

$E^0_{Fe^{3+}/Fe^{2+}} = 0,77V$



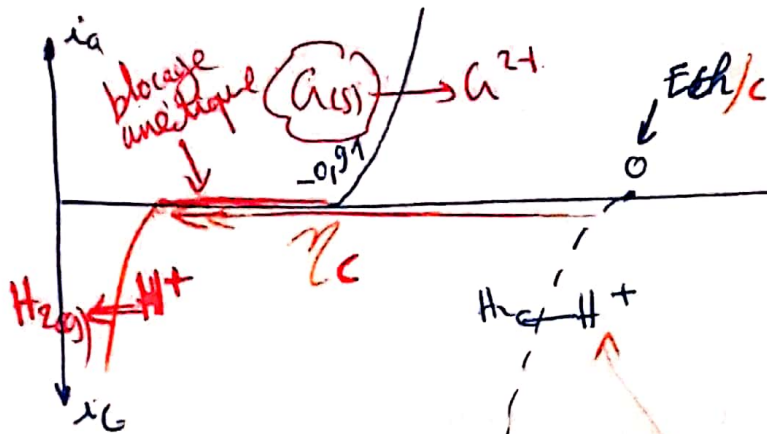
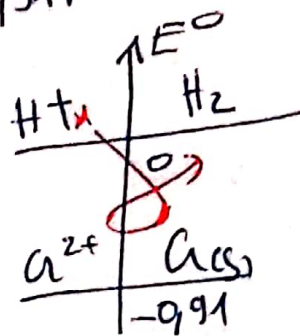
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$$E^{\circ}_{H^+/H_2} = 0V$$

$$E^{\circ}_{Cr^{2+}/Cr} = -0,91V$$

Le chrome est attaqué par l'acide (thermodynamiquement).



experimentalement on n'observe aucun changement de H_2 , système lent.

H^+ reduction $\Rightarrow$ cathode.

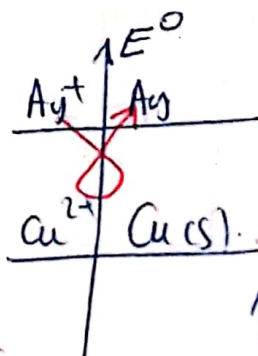
Cr^{2+} oxydation $\Rightarrow$ anode.

Action d'un cation métallique sur un autre métal:

Cimentation

ex $E^{\circ}_{Ag^+/Ag} = 0,71V$

$$E^{\circ}_{Cu^{2+}/Cu} = 0,34$$



Pour que la cimentation soit un échange possible il doit exister un potentiel mixte. ($|I_a| = |I_c|$)

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