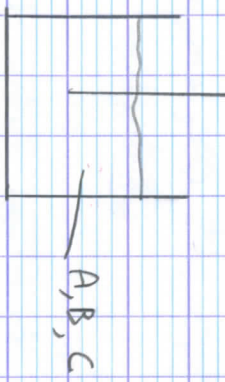


Expérience de mesure:



A, B et C sont dans 1 même électrolyte
 Cette électrode a un potentiel $\frac{1}{2}$ pile
 $E_1 = E_2 = E_3$

ou $E_3 = E_3^0 + \frac{0,06}{m_1 + m_2} \left(\log \frac{[A]}{[B]} + \log \frac{[B]}{[C]} \right)$

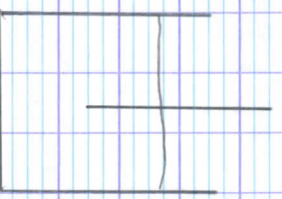
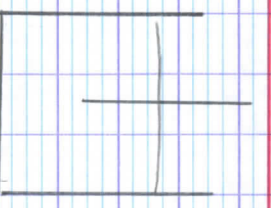
$E_3 = E_3^0 + \frac{0,06}{m_1 + m_2} \left[\frac{m_1}{0,06} (E_1 - E_1^0) + \frac{m_2}{0,06} (E_2 - E_2^0) \right]$

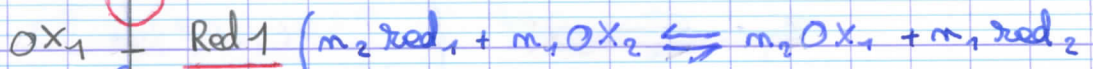
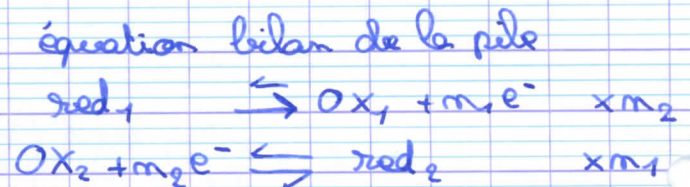
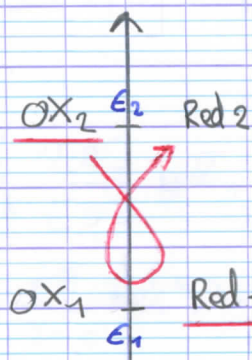
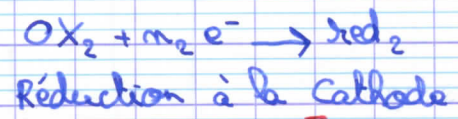
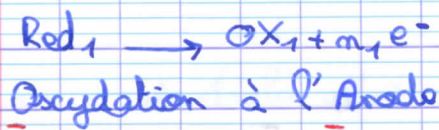
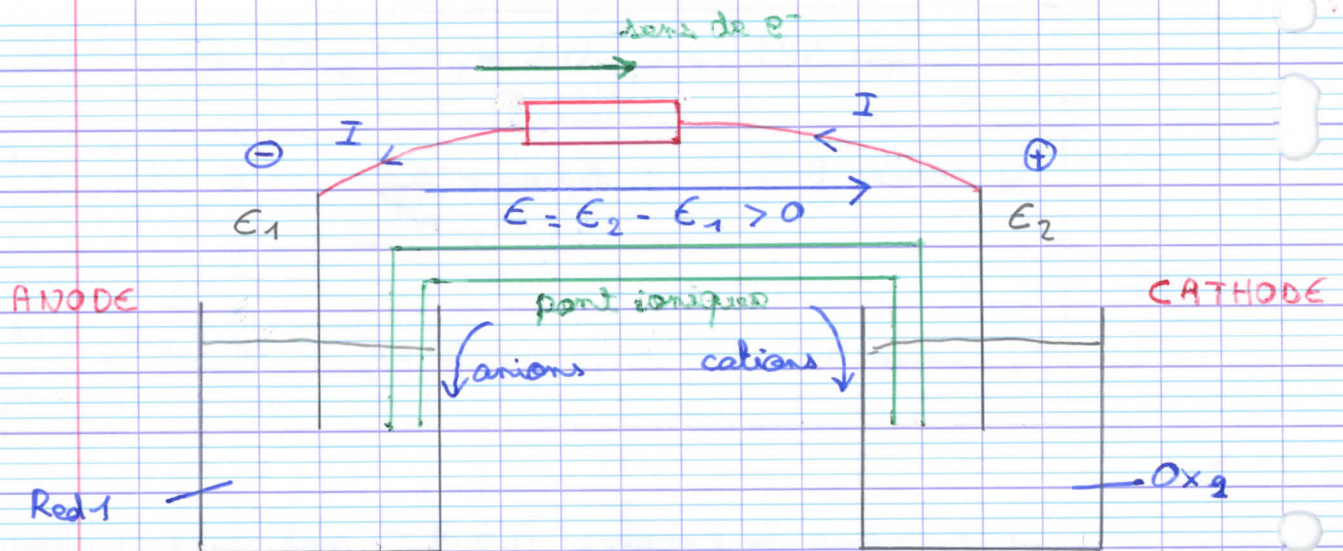
$(m_1 + m_2) E_3 = (m_1 + m_2) E_3^0 + m_1 (E_1 - E_1^0) + m_2 (E_2 - E_2^0)$

$(m_1 + m_2) E = m_1 E + m_2 E + (m_1 + m_2) E_3^0 - m_1 E_1^0 - m_2 E_2^0$

$E_3^0 = \frac{m_1 E_1^0 + m_2 E_2^0}{m_1 + m_2}$

VII Piles électrochimiques (p. 9)





tant que l'équilibre correspondant n'est pas atteint la pile délivre un courant

↳ La constante associée à l'équation bilan :

$$K = \frac{[\text{Ox}_1]^{m_2} [\text{red}_2]^{m_1}}{[\text{red}_1]^{m_2} [\text{Ox}_2]^{m_1}}$$

$$E_1 = E_1^0 + \frac{0,06}{m_1} \log \frac{[\text{Ox}_1]}{[\text{red}_1]}$$

$$E_2 = E_2^0 + \frac{0,06}{m_2} \log \frac{[\text{Ox}_2]}{[\text{red}_2]}$$

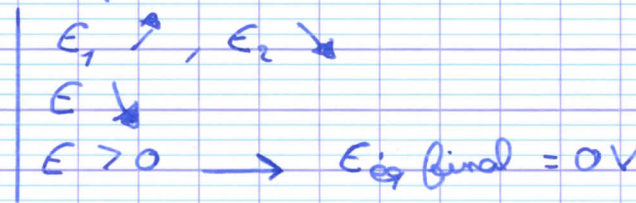
↳ f.e.m de la pile: $E = E_2 - E_1$
 $= E_2^0 - E_1^0 + \frac{0,06}{m_2} \log \frac{[\text{Ox}_2]}{[\text{red}_2]} - \frac{0,06}{m_1} \log \frac{[\text{Ox}_1]}{[\text{red}_1]}$

$$E = E^{\circ} + \frac{0,06}{m_1 m_2} \log \left[\frac{[COX_2]^{m_1} [red_1]^{m_2}}{[red_2]^{m_2} [COX_1]^{m_1}} \right]$$

$$E = E^{\circ} + \frac{0,06}{m_1 m_2} \log \frac{1}{Q}$$

avec $Q \rightarrow K$
 une réaction de quotient Q
 qui évolue vers l'équilibre
 final

Lorsque la pile débite



cl. Lorsque la pile ne débite plus on a

$$E = 0 = E^{\circ} + \frac{0,06}{m_1 m_2} \log \frac{1}{K}$$

↑
 $Q = K$

$$\rightarrow \log K = \frac{E^{\circ} m_1 m_2}{0,06} = \frac{m_1 m_2 (E_2^{\circ} - E_1^{\circ})}{0,06}$$

$$K = 10^{\frac{m_1 m_2 (E_2^{\circ} - E_1^{\circ})}{0,06}}$$

Si on ne travaille pas à 25°C: $\frac{RT}{F} \ln \neq \frac{0,06}{2,3} \log$

alors il faut écrire: $\ln K = \frac{m_1 m_2 E^{\circ} F}{RT}$

Définition:

$$E^{\circ} = E_2^{\circ} - E_1^{\circ}$$

Potential électrochimique standard de la pile