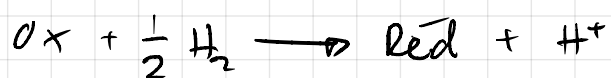


Electrode standard à référence (SHE) H^+/H_2



$$\Delta G_r = -nF\Delta E$$

$\Delta G_r^\circ < 0 \Rightarrow$ spontané de gauche à droite

$$\Rightarrow E^\circ(Ox/Red) > 0$$

$\Delta G_r^\circ > 0 \Rightarrow$ spontané de droite à gauche

$$\Rightarrow E^\circ(Ox/Red) < 0$$

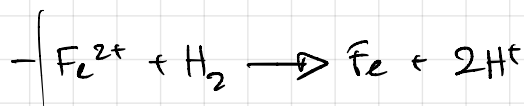
$\Rightarrow$ Le couple dont le pot. E° est le plus élevé oxyde l'autre spontanément $\Rightarrow$ anode

1. Exemple : $E^\circ(Cl_2/Cl^-) = +1.36 V/SHE$

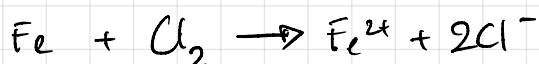
$$E^\circ(Fe^{2+}/Fe) = -0.44 V/SHE$$



$$\Delta G_r^\circ = -E^\circ 2F = -1.36 V \cdot 2F = \underline{-262 kJ/mol}$$



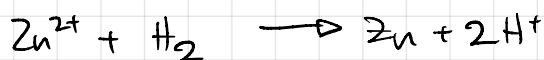
$$\Delta G_r^\circ = -E^\circ 2F = +0.44 V \cdot 2F = \underline{+85 kJ/mol}$$



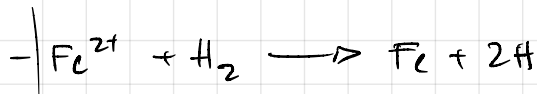
$$\begin{aligned} \Delta G_r^\circ &= -262 kJ/mol - 85 kJ/mol \\ &= \underline{-347 kJ/mol} \end{aligned}$$

réaction spontanée

2. Exemple : $E^\circ(Zn^{2+}/Zn) = -0.76 V/SHE$



$$\Delta G_r^\circ = 0.76 V \cdot 2F = +147 kJ/mol$$



$$\Delta G_r^\circ = +85 kJ/mol$$

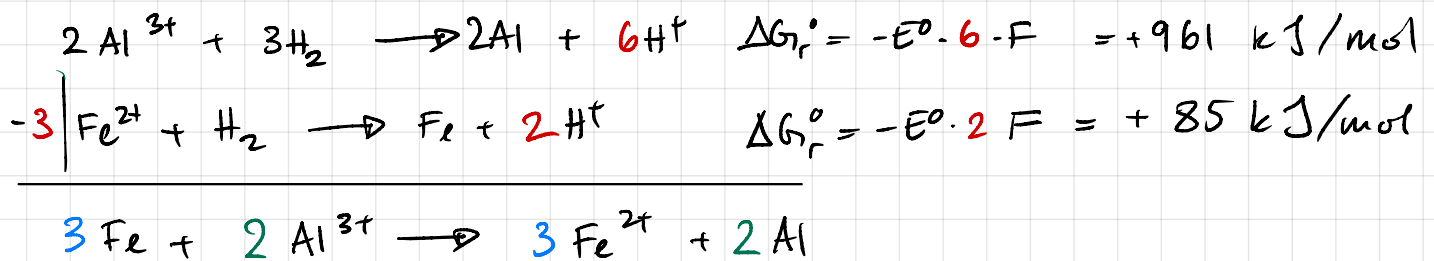
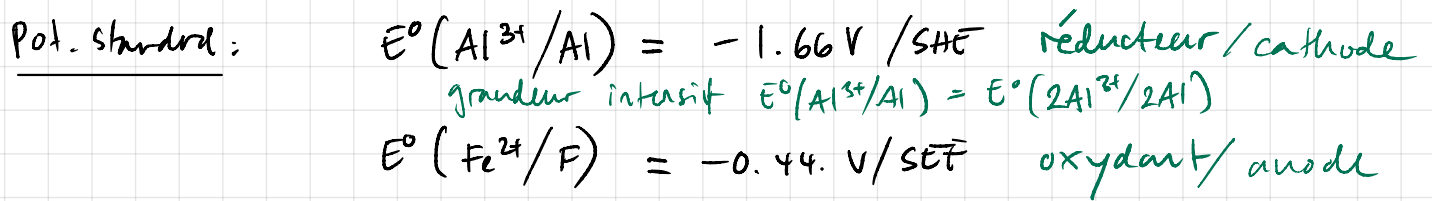
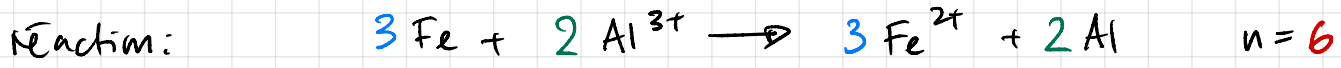


$$\begin{aligned} \Delta G_r &= 147 kJ/mol - 85 kJ/mol \\ &= \underline{62 kJ/mol} \end{aligned}$$

réact. non-spontanée

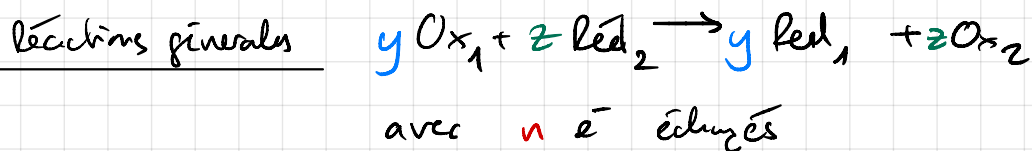
$\rightarrow$ réaction inverse spontanée

Combinaison de 2 demi-piles



Enthalpie libre: $\Delta G_r^\circ = 961 \text{ kJ/mol} - \underbrace{3 \cdot 85 \text{ kJ/mol}}_{\text{mult 3x pour balancer l'équation}} = 706 \text{ kJ/mol}$
(réaction)

F.é.m. : $\Delta E_{\text{pile}}^\circ = \frac{-\Delta G_r^\circ}{6 F} = \underline{\underline{-1.22 \text{ V}}} = E^\circ(\text{Al}^{3+}/\text{Al}) - E^\circ(\text{Fe}^{2+}/\text{Fe})$
(pile)
 $\Rightarrow \left. \begin{array}{l} E^\circ \text{ pot standard} \\ \Delta E^\circ (\text{f.é.m.}) \end{array} \right\} \text{ par mole } e^- \text{ échangé}$



$$\Delta E_{\text{pile}}^\circ = E^\circ(\text{Ox}_1/\text{Red}_1) - E^\circ(\text{Ox}_2/\text{Red}_2)$$

$$\Delta E_{\text{pile}}^\circ = \underbrace{E^\circ_{\text{cathod}}}_{\text{Al}} - \underbrace{E^\circ_{\text{anode}}}_{\text{Fe}}$$

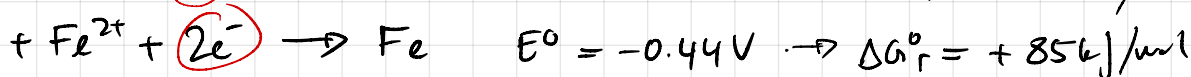
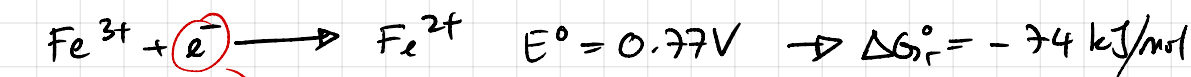
Combinaison de potentiels de demi-réactions

Additivité de E^0 (grandeur intensive)
 → vrai pour les réactions globale (pile)
 → pas vrai pour combinaisons de demi-réactions

Exemple: énergie libre: $\boxed{\text{Fe}^{3+} + \text{Al} \rightleftharpoons \text{Fe} + \text{Al}^{3+}}$?

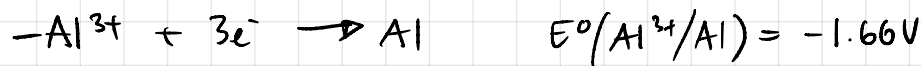
connu: $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$ $E^0(\text{Fe}^{2+}/\text{Fe})$ $E^0(\text{Al}^{3+}/\text{Al})$

connu: $E^0(\text{Fe}^{3+}/\text{Fe})$?



$$E^0(\text{Fe}^{3+}/\text{Fe}) = -\frac{\Delta G_r^0}{\textcircled{3}F} = -\frac{11 \cdot \text{kJ/mol}}{3F} = \boxed{-0.04\text{V}}$$

Fém. de cette pile



$$\Delta E^0 = E^0(\text{Fe}^{3+}/\text{Fe}) - E^0(\text{Al}^{3+}/\text{Al}) = +1.62\text{V}$$

$$\Delta G_r^0 = -\{+1.62\text{V}\} \cdot \textcircled{3}F = \underline{\underline{-469 \text{ kJ/mol}}}$$

⇒ vidéo sur slide

Effet de température

relation ΔG_r° et E° :

$$\Delta G_r^\circ = -nFE^\circ$$

temp. dependence of ΔG_r° ?

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

temperatures T_1, T_2 (faible intervalle $T_1 - T_2$, $\Delta H_r^\circ, \Delta S_r^\circ$ const.)

$$\Delta G_r^\circ(T_2) - \Delta G_r^\circ(T_1) = \cancel{\Delta H_r^\circ} - T_2 \Delta S_r^\circ - \cancel{\Delta H_r^\circ} + T_1 \Delta S_r^\circ = \Delta S_r^\circ (T_1 - T_2)$$

$$\Delta G_r^\circ = -nFE^\circ \rightarrow \Delta G_r^\circ(T_2) - \Delta G_r^\circ(T_1) = -nF[E^\circ(T_2) - E^\circ(T_1)]$$

$$\Rightarrow \Delta S_r^\circ (T_1 - T_2) = -nF[E^\circ(T_2) - E^\circ(T_1)]$$

$$\Rightarrow \Delta S_r^\circ = nF \cdot \frac{E^\circ(T_2) - E^\circ(T_1)}{T_2 - T_1}$$

$\Rightarrow$ déterminer entropie avec un voltamètre !

$$\Delta H_r^\circ = \Delta G_r^\circ + T\Delta S_r^\circ$$