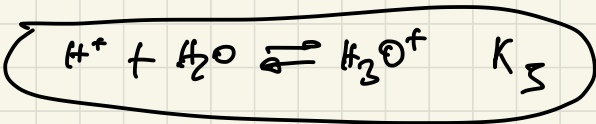
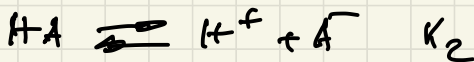
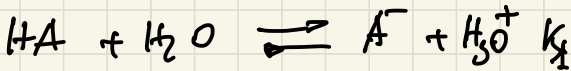


$$pH = -\lg [H^+]$$

$$pE = -\lg \{e^-\}$$

ACTIVITÄT ELECTRONICA

Säure - base



$$\Delta \zeta^0 = 0 \quad K_3 = 1$$

$$K_1 = K_2 \cdot K_3 = K_2$$

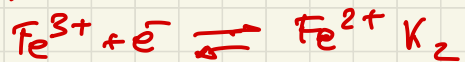
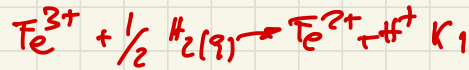
$$K_1 = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = [H^+]$$

$$[H^+] = K_1 \cdot \frac{[HA]}{[A^-]}$$

$$\lg [H^+] = \lg K_1 + \lg \frac{[HA]}{[A^-]}$$

RED - OX



$$\Delta \zeta^0 = 0 \quad K_3 = 1$$

$$K_1 = K_2 \cdot K_3 = K_2 = \frac{[Fe^{2+}]}{[Fe^{3+}][e^-]}$$

$$[e^-] = \frac{[Fe^{2+}]}{[Fe^{3+}] \cdot K_1}$$

$$[e^-] \leftrightarrow [e^-]$$

$$-\lg [e^-] = -\lg \frac{1}{K_1} - \lg \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$- \lg [H^+] = - \lg K_1 - \lg \frac{[HA]}{[A^-]}$$

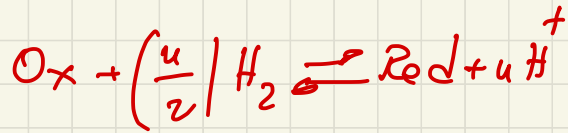
$$pH = pK_1 + \lg \frac{[A^-]}{[HA]}$$

$$- \lg [e^-] = - \lg \frac{1}{K_1} - \lg \frac{[E^{2+}]}{[Fe^{3+}]}$$

$$- \lg [e^-] = \underbrace{\lg K_1}_{pE^\circ} + \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE = \underbrace{(pE^\circ)}_{pE^\circ} + \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE^\circ = \lg K_1$$



$$pE = pE^\circ + \frac{1}{n} \lg \frac{[Ox]}{[Red]}$$

$$pE^\circ = \frac{1}{n} \lg K$$

$$pE = pE^\circ + \frac{1}{n} \lg \frac{\prod [Ox]^{n_i}}{\prod [Red]^{m_j}}$$

$$pE^\circ = \frac{1}{n} \lg K$$

①

 $(pE?)$ 

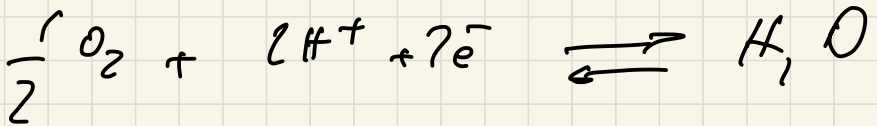
$$pE^0 = \lg K = 13$$

$$pE = pE^0 + \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$\downarrow 13 + \lg \frac{10^{-5}}{10^{-3}} = 11$$

pE?

pH 7.5

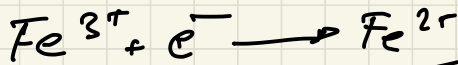


$$\lg K = 41.55$$

$$pE = pE^0 + \frac{1}{2} \lg \left(P_{O_2}^{\frac{1}{2}} \cdot [H^+]^2 \right)$$

$$= 20.78 + \frac{1}{2} \lg \left[0,2 \cdot (10^{-7,5})^2 \right]$$

$$\underline{= 13.43}$$



$$K = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}][e^{-}]}$$

$$F_{\text{Fe}} = [\text{Fe}^{2+}] + [\text{Fe}^{3+}]$$

$$F_{\text{e}^{-}} - [\text{Fe}^{3+}] = [\text{Fe}^{2+}]$$

$$K = \frac{F_{\text{Fe}} - [\text{Fe}^{3+}]}{[\text{Fe}^{3+}][e^{-}]}$$

$$K([\text{Fe}^{3+}] \cdot [e^{-}]) = F_{\text{Fe}} - [\text{Fe}^{3+}]$$

$$F_{\text{Fe}} = K([\text{Fe}^{3+}] \cdot [e^{-}]) + [\text{Fe}^{3+}]$$

$$\begin{aligned} & | \\ & = [\text{Fe}^{3+}] (K \cdot [e^{-}] + 1) \end{aligned}$$

$$[\text{Fe}^{3+}] = \frac{F_{\text{Fe}}}{K \cdot [e^{-}] + 1}$$

divid K

$$\begin{aligned} & | \\ & = \frac{F_{\text{Fe}}/K}{[e^{-}] + \frac{1}{K}} = \frac{F_{\text{Fe}} \cdot K^{-1}}{[e^{-}] + K^{-1}} \end{aligned}$$

$$K = \frac{[Fe^{2+}]}{[Fe^{3+}][e^-]}$$

$$[Fe^{3+}] = F_{Fe} - [Fe^{2+}]$$

$$F_{Fe} = [Fe^{2+}] + [Fe^{3+}]$$

$$K = \frac{[Fe^{2+}]}{(F_{Fe} - [Fe^{2+}]) [e^-]}$$

$$K \cdot [e^-] \cdot (F_{Fe} - [Fe^{2+}]) = [Fe^{2+}]$$

$$K \cdot [e^-] \cdot F_{Fe} - K \cdot [e^-] \cdot [Fe^{2+}] = [Fe^{2+}]$$

$$[Fe^{2+}] (1 + K \cdot [e^-]) = K [e^-] \cdot F_{Fe}$$

$$[Fe^{2+}] = \frac{K \cdot [e^-] \cdot F_{Fe}}{1 + K \cdot [e^-]} \quad \text{dividiere}$$

$$\frac{K [e^-] \cdot F_{Fe}}{K}$$

$$\frac{1 + K [e^-]}{K}$$

$$[Fe^{2+}] = \frac{[e^-] \cdot F_{Fe}}{\frac{1}{K} + [e^-]} = \frac{F_{Fe} \cdot [e^-]}{[e^-] + K^{-1}}$$

$$pE = pE^0 + \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE^0 = \lg K_1$$

$$\lg C - pE$$

$$[Fe^{2+}] = \frac{Fe_T \cdot [e^-]}{[e^-] + K^{-1}} \quad [Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{[e^-] + K^{-1}}$$

$$[e^-] \gg K^{-1}$$

$$[Fe^{2+}] = \frac{Fe_T \cdot [e^-]}{[e^-]} \approx Fe_T$$

$$pE = pE^0 + \lg \frac{[Fe^{3+}]}{Fe_T}$$

$$\lg [Fe^{3+}] = \lg Fe_T + pE - pE^0$$

$$\lg [Fe^{2+}] \approx \lg Fe_T$$

$$[e^-] \ll K^{-1}$$

$$[Fe^{2+}] = \frac{Fe_T \cdot [e^-]}{[e^-] + K^{-1}} \quad [Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{[e^-] + K^{-1}}$$

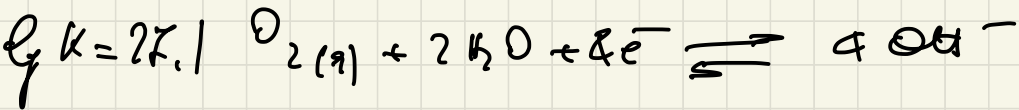
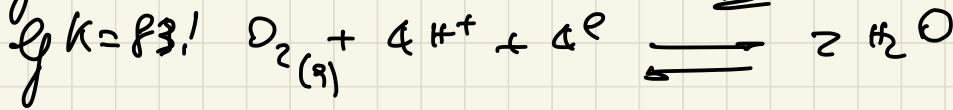
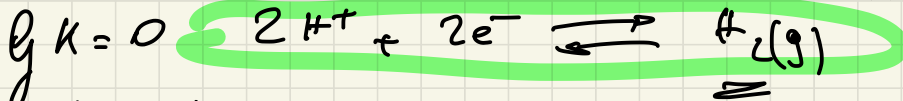
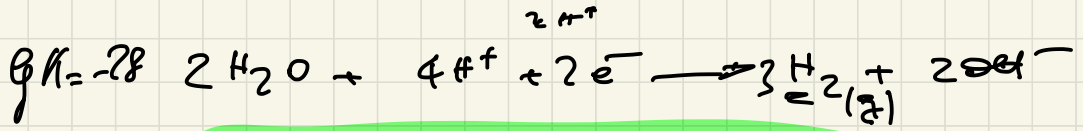
$$[Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{K^{-1}} \approx Fe_T$$

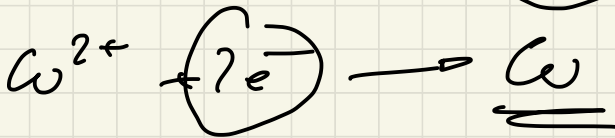
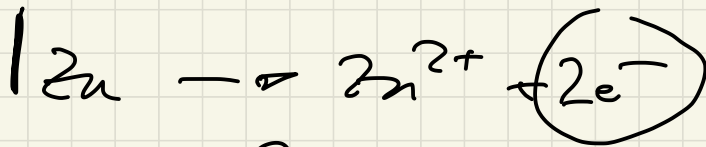
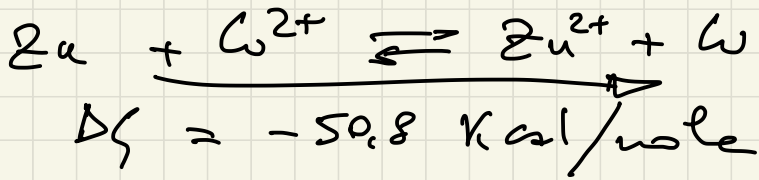
$$\lg [Fe^{3+}] \approx \lg Fe_T$$

$$pE = pE^0 + \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE = pE^0 + \lg \frac{Fe_T}{[Fe^{2+}]}$$

$$\lg [Fe^{2+}] = \lg Fe_T + pE^0 - pE$$





ΔE

ΔG^0

$$E^0 \frac{Cu}{Cu^{2+}} = +0.34 \text{ V}$$

$$E^0 \frac{Zn}{Zn^{2+}} = -0.76 \text{ V}$$

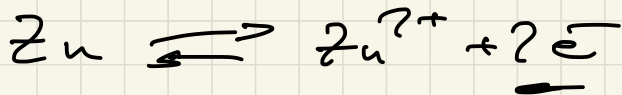
$$\frac{\Delta G^0}{\Delta E^0} \quad \Delta E^0$$

$$\Delta E = \frac{n_0}{nF}$$

$$\Delta G = -nF \Delta E$$

$$W_0 = -\Delta G$$

$$\Delta E = -\frac{\Delta G}{nF}$$



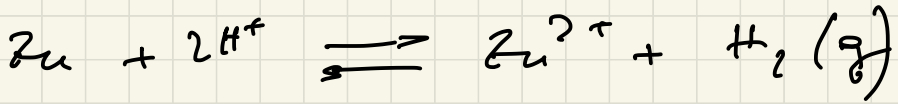
$$K = \frac{[Zu^{2+}]}{[Zu]} \quad u=2$$

$$E = E_{H^+}^0 + \frac{2.3025 (RT)}{2F} \lg [Zu^{2+}]$$

25°C

$$E = E_{H^+}^0 + \frac{0.0592}{2} \lg [Zu^{2+}]$$

$$E = E_{H^+}^0 + 0.0296 \lg [Zu^{2+}]$$



$$E = E^\circ + \frac{0,0592}{2} \lg \frac{[\text{Cu}^{2+}]^2}{[\text{H}^+]^2}$$

25°C $n=2$

$\lg \frac{[\text{Cu}^{2+}]^2}{[\text{H}^+]^2}$

\downarrow
 $\lg 17$

$$= E^\circ + \frac{0,0592}{2} \lg [\text{Cu}^{2+}]$$

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

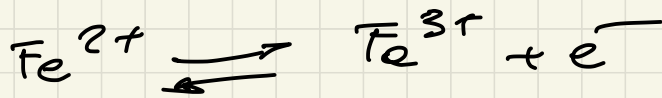
$$\Delta G^\circ = -RT \ln K_L$$

$$pE^\circ = \frac{1}{n} \lg K_L$$

$$\lg K_L = -\frac{\Delta G^\circ}{RT \cdot 2,3}$$

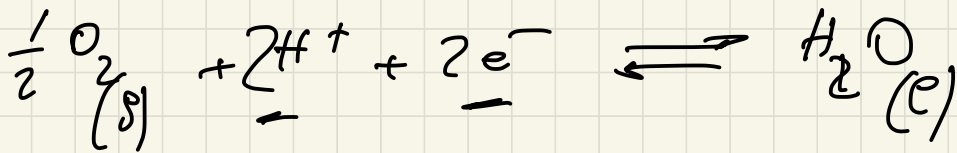
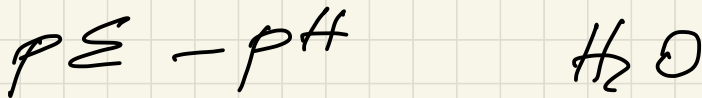
$$= \frac{1}{n} \frac{-\Delta G^\circ}{2,3RT} = \frac{1}{n} \cdot \frac{nFE^\circ}{2,3RT}$$

$$pE^\circ = \frac{F}{2,3RT} E^\circ$$



$$pE = pE^{\circ} + \lg \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$K = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$



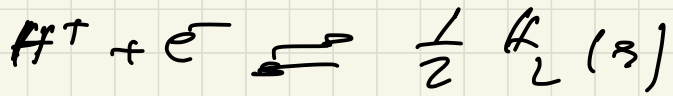
$$E_{\text{H}}^{\circ} = 1.23 \text{ V}$$

$$E_{\text{H}} = E_{\text{H}}^{\circ} + 0.0295 \lg \frac{p_{\text{O}_2}^{1/2} [\text{H}^{+}]^2}{1}$$

$$E = 1.23 + 0.0148 \lg p_{\text{O}_2} - 0.059 pH$$

$$E = 1.23 - 0.059 pH$$

(1)

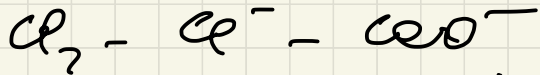


$$E_H = \cancel{E^\circ} + 0,059 \lg \left(\frac{[H^+]}{p_{H_2}^{1/2}} \right)$$

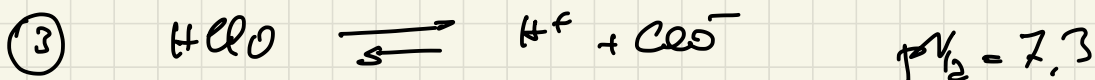
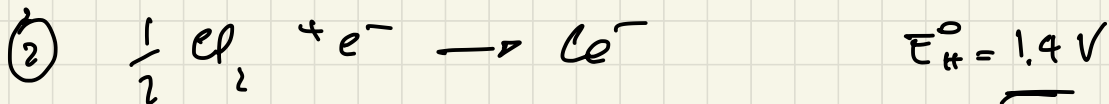
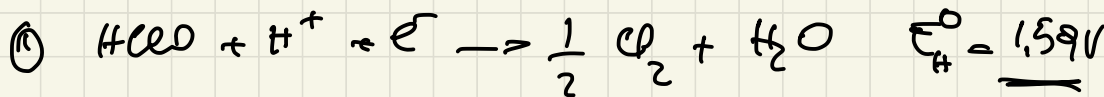
↑
poten

$$E = -0,059 pH$$

$$\bar{E}_H \sim pH$$

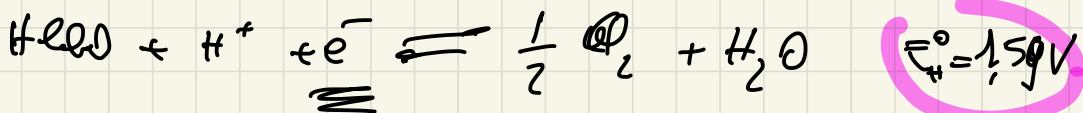


$$Cl^- = 10^{-4} M$$



$$Cl^- = 10^{-4} M = 2[Cl_2] + [HClO] + [ClO^-] + [Cl^-]$$

combine $HClO/Cl_2$



$$E = E_H^0 - \frac{0.0592}{1} \log \frac{[Cl_2]^{1/2}}{[H^+][HClO]}$$

$$\text{if combine } [Cl_2] = [HClO]$$

$$E = E_H^{\circ} - \frac{0,0592}{1} \log \frac{[Cl_2]_4^{\frac{1}{2}}}{[H^+][HClO]}$$

al coefficient $[Cl_2] = [HClO]$

$$2[Cl_2] + [HClO] \Rightarrow [ClO^-] + [Cl^-]$$

$$2[Cl_2] + [HClO] = 10^{-4} M = C_{PT}$$

$$3[Cl_2] = 10^{-4} M$$

$$[Cl_2] = 3,3 \cdot 10^{-5} M.$$

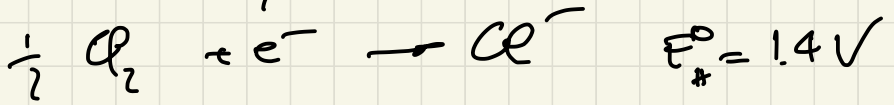
$$\begin{aligned} [HClO] &= C_{PT} - 2[Cl_2] = 10^{-4} - 2(3,3 \cdot 10^{-5}) \\ &= \underline{3,3 \cdot 10^{-5}} \end{aligned}$$

$$E = 1,59 - \frac{0,0592}{1} \log \frac{(3,3 \cdot 10^{-5})^{\frac{1}{2}}}{[H^+] \cdot 3,3 \cdot 10^{-5}}$$

$$= 1,59 - 0,0592 \log \frac{174}{[H^+]}$$

$$E = 1,46 - 0,0592 \text{ pH}$$

continue Cl_2/Cl^-



$$E = E^\circ - \frac{0.0592}{1} \log \frac{[\text{Cl}^-]}{[\text{Cl}_2]^{1/2}}$$
$$= 1.4 - 0.0592 \log \frac{(3.3 \cdot 10^{-5})}{(3.3 \cdot 10^{-5})^{1/2}}$$

$$[\text{Cl}^-] = [\text{Cl}_2] \quad \underline{\text{def. coefficient}}$$

$$2[\text{Cl}_2] + [\text{Cl}^-] \gg [4\text{ClO}] + [\text{ClO}]$$

$$2[\text{Cl}_2] + [\text{Cl}^-] = 10^{-4} \text{ M} = C_T$$

$$3[\text{Cl}_2] = 10^{-4} \Rightarrow [\text{Cl}_2] = 3.3 \cdot 10^{-5} \text{ M}$$

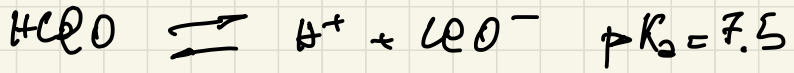
$$[\text{Cl}^-] = C_T - 2[\text{Cl}_2]$$

$$\stackrel{!}{=} 10^{-4} - 2(3.3 \cdot 10^{-5}) = 3.3 \cdot 10^{-5} \text{ M}$$

$$E = E^\circ - \frac{0.0592}{1} \log \frac{[\text{Cl}^-]}{[\text{Cl}_2]^{1/2}}$$
$$= 1.4 - 0.0592 \log \frac{(3.3 \cdot 10^{-5})}{(3.3 \cdot 10^{-5})^{1/2}}$$

$$E = 1.4 - 0.0592 \log (5.75 \cdot 10^{-3}) = 1.53$$
$$E = 1.53$$

Calc. $\text{HClO} / \text{ClO}^-$



$$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]}$$

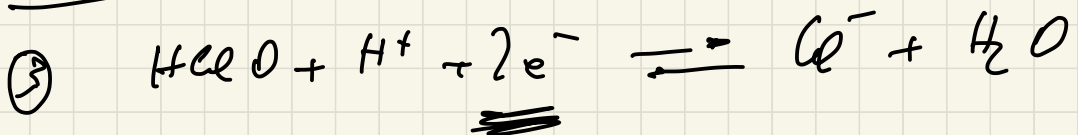
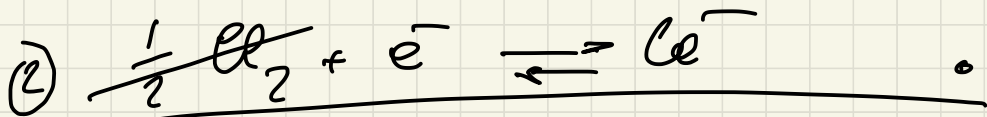
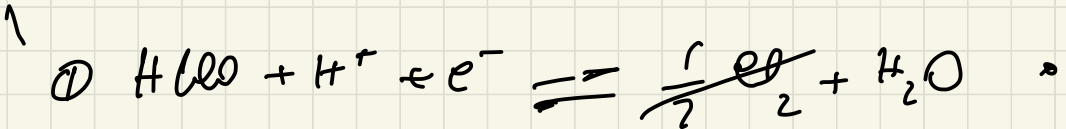
$$[\text{H}^+] = \frac{K_a \cdot [\text{HClO}]}{[\text{ClO}^-]}$$

Calc. $[\text{ClO}^-] = [\text{HClO}]$

$$[\text{H}^+] = K_a$$

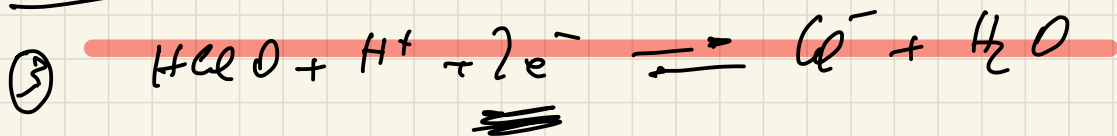
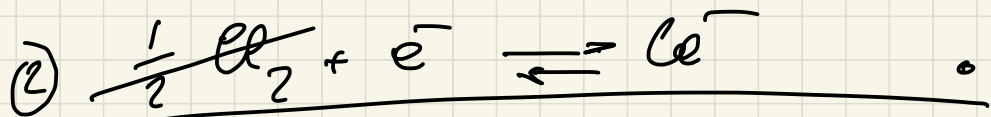
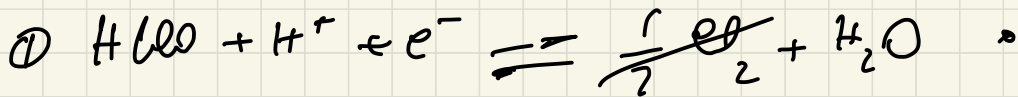
$$\text{pH} = \text{p}K_a = 7.5$$

Calc. $\text{HClO} / \text{Cl}^-$



$$E^\circ ?$$

$$\Delta G^\circ_{\textcircled{3}} = \Delta G^\circ_{\textcircled{1}} + \Delta G^\circ_{\textcircled{2}}$$



$$E_{\#}^{\circ} = 1,5 \text{V}$$

$$\Delta G_{\textcircled{3}}^{\circ} = \Delta G_{\textcircled{1}}^{\circ} + \Delta G_{\textcircled{2}}^{\circ}$$

$$u_3 \cdot E_{\#3}^{\circ} = u_1 \cdot E_{\#1}^{\circ} + u_2 \cdot E_{\#2}^{\circ}$$

$$E_{\#3}^{\circ} = \frac{u_1 \cdot E_{\#(1)}^{\circ} + u_2 \cdot E_{\#(2)}^{\circ}}{u_3}$$

$$E_{\#3}^{\circ} = \frac{1,59 + 1,40}{2} = 1,5 \text{V}$$

$$E_3 = E_{\#3}^{\circ} - \frac{0,0592}{2} \cdot \lg \frac{[\text{Cl}^-]}{[\text{H}^+][\text{HClO}]}$$

$$\text{cond. def.} \Rightarrow \underline{[\text{Cl}^-]} = \underline{[\text{HClO}]}$$

$$C_{Cl^-} = 10^{-4} = (Cl^-) + [HClO] \gg 2[ClO^-] + [ClO^-]$$

$$2[ClO^-] = 10^{-4} \text{ M} \quad [ClO^-] = 5 \cdot 10^{-5} \text{ M}$$

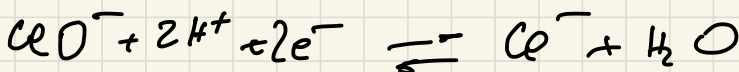
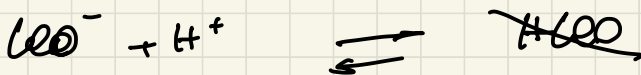
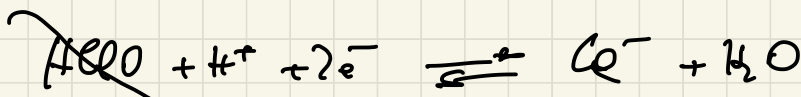
$$[HClO] = C_{Cl^-} - [ClO^-] = 10^{-4} - 5 \cdot 10^{-5} \\ = 5 \cdot 10^{-5} \text{ M}$$

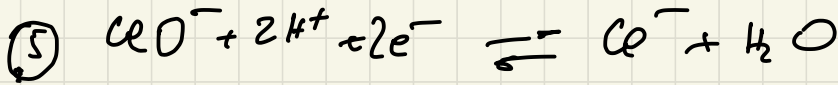
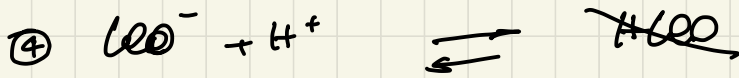
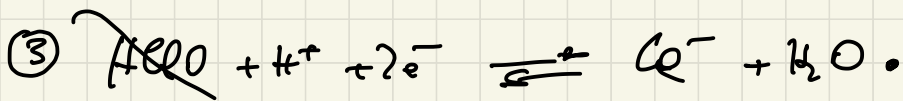
$$E_3 = E_{H_3}^0 - \frac{0,0592}{2} \cdot \lg \frac{[ClO^-]}{[H^+][HClO]}$$

$$= 1,5 - \frac{0,0592}{2} \cdot \lg \frac{5 \cdot 10^{-5}}{[H^+] \cdot 5 \cdot 10^{-5}}$$

$$E = 1,5 - 0,29 \text{ pH}$$

Confinue ClO^-/Cl^-





$$\Delta S_5^0 = \Delta S_3^0 + \Delta S_4^0$$

$$n_5 \cdot F \cdot E_{\text{H}_5}^0 = n_3 \cdot F \cdot E_{\text{H}_3}^0 + RT \ln K_4$$

$$E_{\text{H}_5}^0 = \frac{n_3 \cdot F \cdot E_{\text{H}_3}^0}{n_5 \cdot F} + \frac{RT \ln K_4}{n_5 \cdot F}$$

$$= \frac{2 \cdot 1.5}{2} + \frac{0.0592}{2} \log(10^{-2.5})$$

$$E_{\text{H}_5}^0 = 1.28 \text{ V}$$

$$E_S = E_{\text{H}_5}^0 - \frac{0.0592}{2} \log \frac{[\text{CO}^-]}{[\text{H}^+]^2 \cdot [\text{COO}^-]}$$

$$[\text{CO}^-] + [\text{COO}^-] \gg 2[\text{CO}_2] + [\text{HCOO}^-] = 10^{-4}$$

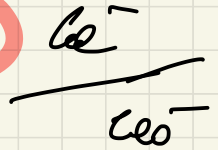
$$2[\text{CO}^-] = 10^{-4}$$

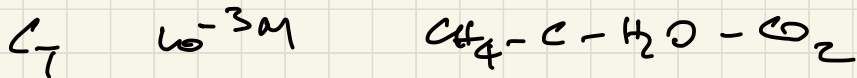
$$[\text{CO}^-] = 5 \cdot 10^{-5}$$

$$[\text{Co}^{2+}] = c_{\text{Co}} - [\text{Co}^{3+}] = 5^{-4} - 5 \cdot 10^{-5} = 5 \cdot 10^{-5}$$

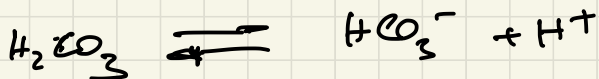
$$E_s = E_{\text{H}_2\text{S}}^0 - \frac{0,0592}{2} \lg \frac{5 \cdot 10^{-5}}{[\text{H}^+]^2 \cdot 5 \cdot 10^{-5}}$$

$$E_s = 1,28 - 0,592 \text{ pH}$$





H_2CO_3 / HCO_3^- Confini



$$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$[H_2CO_3] = [HCO_3^-]$$

$$[H^+] = K_{a1} \frac{[H_2CO_3]}{[HCO_3^-]}$$

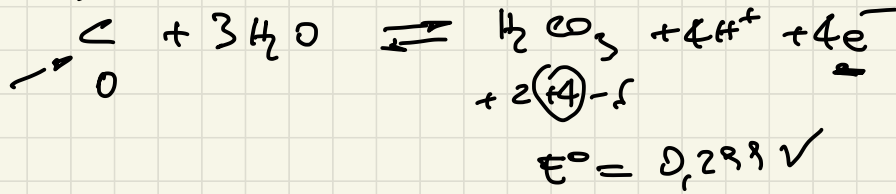
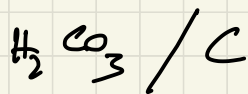
$$pH = -\log K_{a1} = 6,4$$

HCO_3^- / CO_3^{2-} Confini



$$[CO_3^{2-}] = [HCO_3^-] \quad K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$pH = -\log K_{a2} = 10,3$$



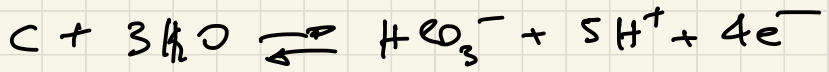
$$E = E^\circ_{\text{H}} + \frac{0,0592}{4} \lg \frac{[\text{H}^+]^4 \cdot [\text{H}_2\text{CO}_3]}{[\text{C}]}$$

$$c_T = \sum c \approx [\text{H}_2\text{CO}_3] = 10^{-3} \text{ M}$$

$$= 0,299 + \frac{0,0592}{4} \lg (10^{-3}) - 0,0592 \cdot \text{pH}$$

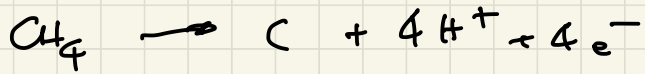
$$E = 0,184 - 0,0592 \text{ pH}$$

$\text{HCO}_3^- / \text{C} (\text{pH} \approx 7)$ Cathode $E_H^0 = 0,324 \text{ V}$



$$C_T = \sum C \approx [\text{HCO}_3^-] = 10^{-3} \text{ M}$$

$$\begin{aligned} E_H &= E_H^0 + \frac{0,0592}{4} \lg \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]^5}{[\text{C}]} \\ &= 0,324 + \frac{0,0592}{4} \lg(10^{-3}) - \frac{0,0592}{4} \cdot 5 \text{ pH} \\ E_H &= 0,28 - 0,074 \text{ pH} \end{aligned}$$



(+4)

(0)

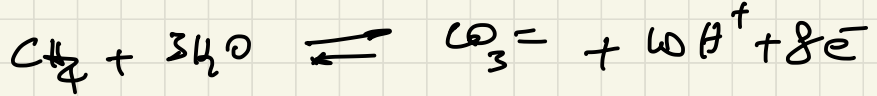
$$E^{\circ} = 0,0898 \text{ V}$$

$$[\text{CH}_4] = [\text{C}] = [\text{H}^+] = 10^{-3} \text{ M}$$

$$E = E^{\circ} + \frac{0,0592}{4} \log \frac{[\text{H}^+]^4 \cdot [\text{C}]}{[\text{CH}_4]}$$

$$= 0,0898 + \frac{0,0592}{4} \log (10^3) - \frac{0,0592}{4} \log 10^3$$

$$E = 0,134 - 0,0592 \text{ pH}$$



$$E^\circ = 0,283 \text{ V}$$

$$E = E^\circ + \frac{0,0592}{8} \log \frac{[\text{H}^+]^4 [\text{CO}_2]}{[\text{CH}_4] [\text{H}_2\text{O}]^2}$$

$[\text{CH}_4] = [\text{CO}_2]$

$$= 0,283 + \frac{0,0592}{8} + \frac{0,0592}{8} \log [\text{H}^+]^4$$

$$= 0,283 - 0,074 \text{ pH}$$