

$$E = E^\circ + \frac{0,06}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2}$$

$$E = E^\circ + \underbrace{0,01 \log \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2}}_{\text{cte}} - 0,14\text{pH}$$

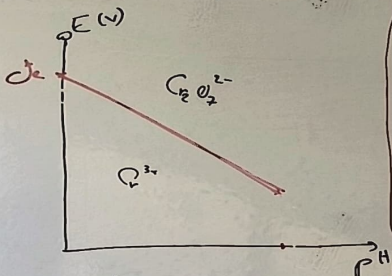
Convention sur la distribution

$$\begin{cases} 2[\text{Cr}_2\text{O}_7^{2-}] = [\text{Cr}^{3+}] \\ 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{Cr}^{3+}] = C_{\text{Tcr}} \end{cases}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = \frac{C_{\text{Tcr}}}{4}$$

$$[\text{Cr}^{3+}] = \frac{C_{\text{Tcr}}}{2}$$

$$E = E^\circ + 0,01 \log C_{\text{Tcr}} - 0,14\text{pH}$$



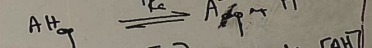
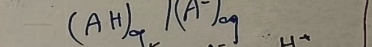
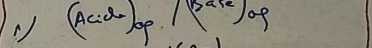
$$\text{p}K_e = -\log K_e ; K_e = [\text{H}^+] \cdot [\text{OH}^-]$$

$$\text{p}K_e = -\log K_a : \text{AH} \rightleftharpoons \text{A}^- + \text{H}^+$$

$$\text{p}K_s = -\log K_s : \text{M}(\text{OH})_m \rightleftharpoons \text{M}^{m+} + m(\text{OH}^-)$$

$$K_a : (\text{AH})_q / (\text{A}^-)_q \quad K_s : \text{M}^{m+} / \text{M}(\text{OH})_m$$

2) distribution acide/base



$$K_e = \frac{[\text{A}^-]_q [\text{H}^+]_q}{[\text{AH}]_q} \Leftrightarrow [\text{H}^+] = \frac{K_a \cdot [\text{AH}]}{[\text{A}^-]}$$

$$-\log[\text{H}^+] = -\log K_e + \log \frac{[\text{A}^-]}{[\text{AH}]}$$

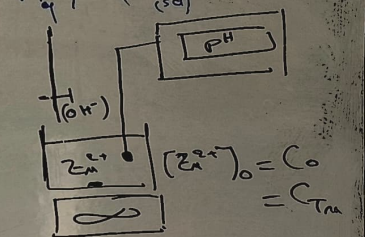
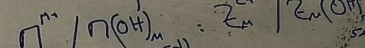
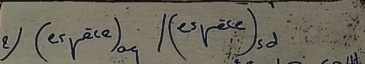
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{AH}]}$$

Sur la distribution: $[\text{AH}]_q = [\text{A}^-]_q$

$$\Rightarrow \text{pH} = \text{pH}_{\text{lim}} = \text{p}K_e$$

dominance de AH / dominance de A^-

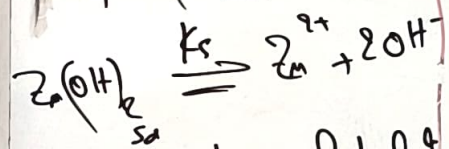
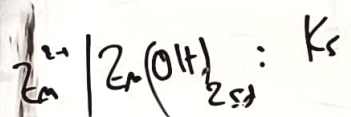
$$[\text{AH}] > [\text{A}^-] \quad \text{pH} < \text{p}K_e \quad [\text{A}^-] > [\text{AH}] \quad \text{pH} > \text{p}K_e$$



Au début de la précipitation

$$[\text{Zn}^{2+}]_i = C_0 = C_{\text{Tcr}}$$

$$\text{pH} = \text{pH}_{\text{lim}}$$



K_s : produit de solubilité

$$K_s = [Zn^{2+}]_e [OH^-]^2$$

$$K_s = C_{T_{Zn}} \cdot \frac{K_e}{[H^+]^2}$$

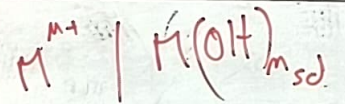
$$[H^+] = \left(C_{T_{Zn}} \cdot \frac{K_e}{K_s} \right)^{1/2}$$

$$-\log([H^+]) = -\frac{1}{2} \log \frac{C_{T_{Zn}} \cdot K_e}{K_s}$$

$$pH_{lin} = pK_e - \frac{1}{2} (\log C_{T_{Zn}} + pK_s)$$

donnée de Zn^{2+} prédominance $Zn(OH)_2$ pH

$$[Zn^{2+}] = C_{T_{Zn}} \cdot 10^{pH_{lin}} [Zn^{2+}]_e = \sum = \frac{K_s}{[OH^-]^2}$$



$$pH_{lin} = pK_e - \frac{1}{m} (\log C_m + pK_s)$$

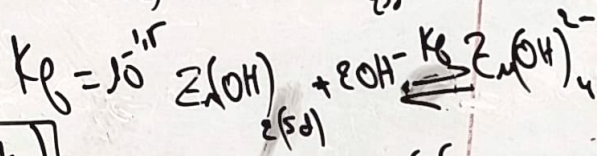
III construction du diagramme E-pH ($Zn^{2+} : Zn$)

espèces présentes en solution aqueuse: Zn^{2+} , $Zn(OH)_2$

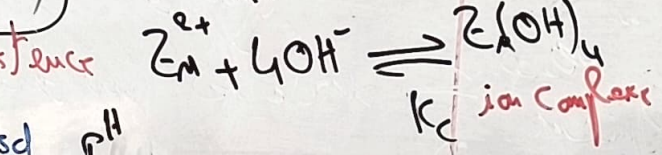
on donne $T = 298$ $Zn(OH)_2$

$$K_e : 10^{-14} : H_2O \rightleftharpoons H^+ + OH^-$$

$$K_s(Zn(OH)_2) = 10^{-17} : Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$$



$$K_c(Zn(OH)_4^{2-}) = 10^{11.17}$$



ion complexe

équilibre de complexation: $K_c(B)$
 $M + mL \rightleftharpoons M(L)_m$
 cation métallique Complexe

$$K_c = \frac{[M(L)_m]_e}{[M]_e [L]_e^m}$$

$$C_{T_{Zn}} = 10^{-2} \text{ mol.L}^{-1}$$

$$E^0(Zn^{2+}/Zn) = -0.76V$$

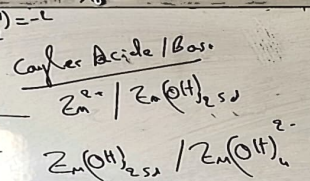
m.o (Zn) dans les différents espèces.

$$x + y(-1) = -2$$

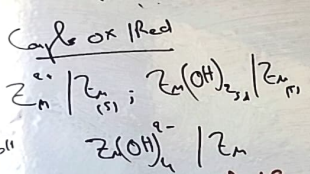
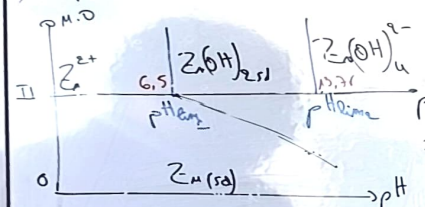
$$x + 2(-1) = 0$$

$$x = 2$$

espèces	Zn^{2+}	Zn^{2+}	$Zn(OH)_2$	$Zn(OH)_4^{2-}$
m.o (Zn)	0	II	II	II



2/ Coupler acide / Base ; Coupler ox / Red



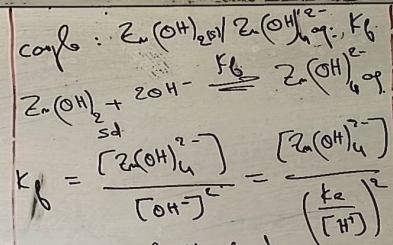
la valeur du pH ? la charge de couple $Zn^{2+} / Zn(OH)_2$: l'espèce

3/ des fonctions acide / Base

$$Zn(OH)_2 \xrightleftharpoons{K_s} Zn^{2+} + 2OH^-$$

$$pH_{lim} = pK_s - \frac{1}{2} (\log C_{T_{Zn}} + pK_s)$$

$$pH_{lim} = 6.5$$



Convention sur la dtz fonction

$$[Zn(OH)_4^{2-}]_{eq} = C_{T_{Zn}}$$

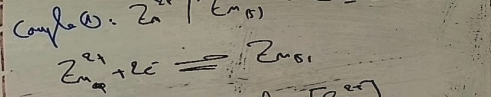
$$K_b = \frac{C_{T_{Zn}} [H^+]^2}{K_w^2}$$

$$[H^+] = \left(\frac{K_b \cdot K_w^2}{C_{T_{Zn}}} \right)^{1/2}$$

$$[H^+] = \left(\frac{10^{-14} \cdot 10^{-28}}{10^{-2}} \right)^{1/2} = 10^{-13.7}$$

$$pH_{lim} = 13.7$$

4/ des fonctions ox / Red



$$E_1 = E^0 + \frac{0.06}{n} \log [Zn^{2+}]$$

Convention sur la dtz fonction ox / Red

$$[Zn^{2+}] = C_{T_{Zn}}$$

$$E_1 = E^0 + 0.03 \log C_{T_{Zn}} = -0.76 - 0.06$$

$$E_{Zn^{2+}/Zn} = -0.82V$$

Compte ②: $Zn(OH)_2 \text{ sat} / Zn_{(sd)}$ 2^{ème} méthode
 $Zn(OH)_2 \text{ sat} + 2e^- + 2H^+ \rightleftharpoons Zn_{(sd)} + 2H_2O$ sur la dté française $Zn(OH)_2 / Zn$

$$E_2 = E_2^0 + \frac{0,06}{2} \log [H^+]^2$$

les espèces présentes : $Zn_{(sd)}$, $Zn(OH)_2 \text{ sat}$ et Zn^{2+}

$$E_2 = E_2^0 - 0,06 \text{ pH} \quad (Zn^{2+} / Zn) \text{ espèce libre } (Zn(OH)_2 / Zn)$$

1^{ère} méthode

Condition de calcul: de $E_{Zn^{2+}/Zn} = E_{Zn(OH)_2 \text{ sat}/Zn}$
 Potentiel à $\text{pH}_{lim} = 6,1$

$$E(Zn^{2+}/Zn) = E_{Zn(OH)_2 \text{ sat}/Zn}$$

$$-0,82 = E_2^0 - 0,06(6,1)$$

$$E_2^0 = -0,82 + 0,06(6,1)$$

$$E_2^0 = -0,43$$

$$E_1^0 + 0,03 \log [Zn^{2+}] = E_2^0 + 0,03 \log [H^+]^2$$

$$E_2^0 = E_1^0 + 0,03 \log \frac{[Zn^{2+}]}{[H^+]^2} = E_1^0 + 0,03 \log \frac{[Zn^{2+}][OH^-]^2}{[H^+][OH^-]}$$

$$E_2^0 = E_1^0 + 0,03 \log \frac{K_s}{K_e} = -0,43 \text{ V}$$

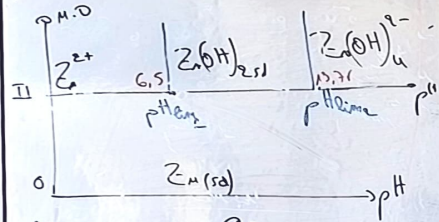
$$E_{Zn(OH)_2/Zn} = -0,43 - 0,06 \text{ pH}$$

1/ m.o (Zn) dans les différents espèces.

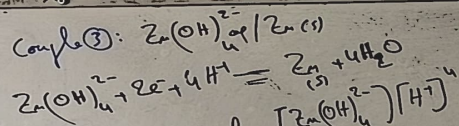
$z + e(z_{eq}) = 0$

espèces	$Z_{m(s)}$	Z_m^{2+}	$Z(OH)_2(s)$	$Z(OH)_4^{2-}$
m.o (Zn)	0	II	II	II

2/ Complexes acide / Base ; Complexes ox / Red



la valeur du pH ? la charge de l'espèce ↓



$$E_3 = E_3^0 + \frac{0,06}{2} \log [Zn(OH)_4^{2-}] [H^+]^4$$

$$E_3 = E_3^0 + 0,03 \log [Zn(OH)_4^{2-}] - 0,12 \text{ pH}$$

Conversion en l'unité française ②

$$[Zn(OH)_4^{2-}] = C_{Tn}$$

$$E_3 = E_3^0 + 0,03 \log (C_{Tn} - 0,12 \text{ pH})$$

1^{re} méthode : Calcul de concentration de potentiel à $pH_{lim2} = 13,78$

$$E_2(pH_{lim2}) = E_3(pH_{lim2})$$

$$-0,43 - 0,06 (13,78) = E_3^0 + 0,03 \log 10^{-2} - 0,12 (13,78)$$

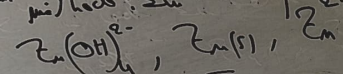
$$E_3^0 = -0,43 + 13,78 (0,12 - 0,06) - 0,03 \log 10^{-2}$$

$$E_3^0 = 0,477 \text{ V}$$

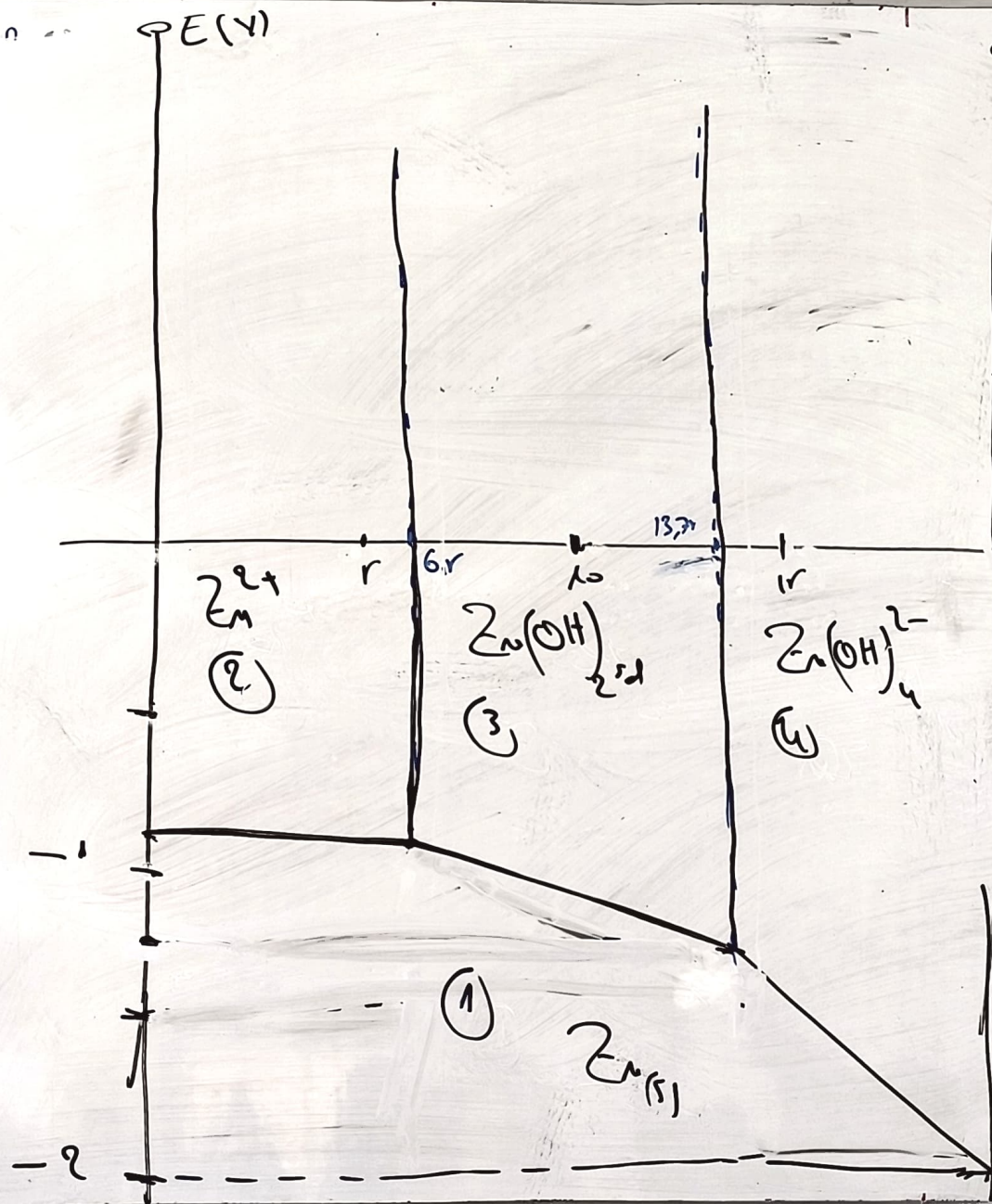
$$E_{Zn(OH)_4^{2-} / Zn} = 0,477 + 0,03 \log 10^{-2} - 0,12 \text{ pH}$$

$$E_{Zn(OH)_2 / Zn} = 0,395 - 0,12 \text{ pH}$$

2^{de} méthode : Sur l'unité française ③



$$E_{Zn^{2+} / Zn} = E_{Zn(OH)_4^{2-} / Zn}$$



$$E_2(pH=13.7) = -1.86$$

$$E_3(pH=20) = -$$

domaine (1): domaine d'existence de $Zn(s)$

domaine (2): domaine de prédominance de Zn^{2+}

domaine (3): domaine d'existence de $Zn(OH)_2(s)$

domaine (4): domaine de prédominance de $Zn(OH)_4^{2-}$

