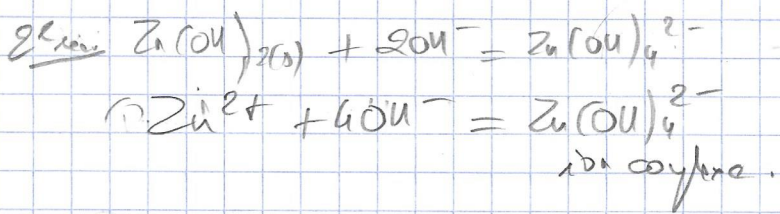
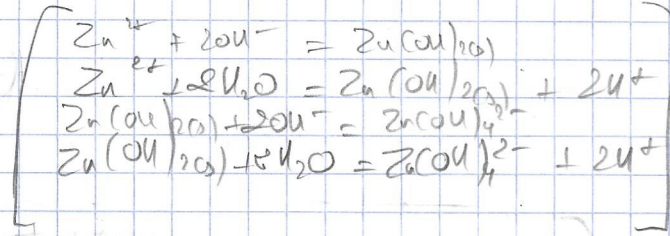
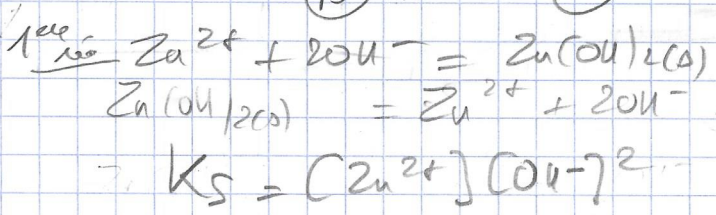
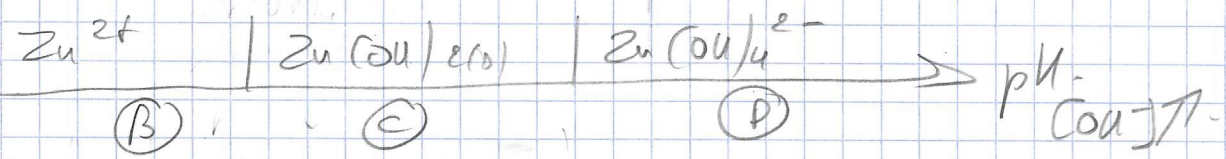
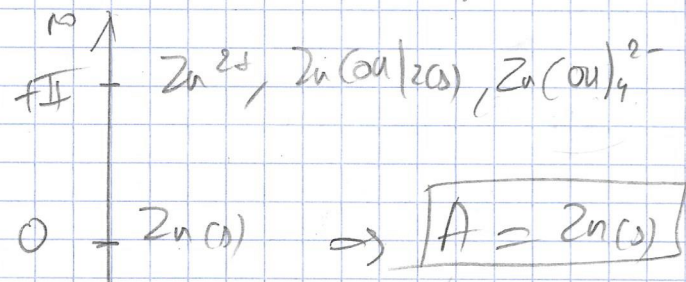


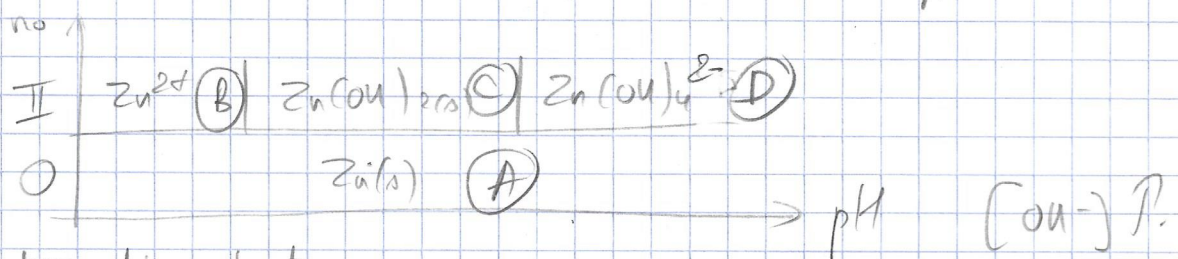
IV Lecture de diagrammes

Exemple: Diagramme du zinc  $C_T = 10^{-2} \text{ mol.l}^{-1}$   
 etude préliminaire

Esigees:  $Zn, Zn^{2+}, Zn(OH)_2(s), Zn(OH)_4^{2-}$  ion complexe



$B_4 = \frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4}$   
 constante globale de formation du complexe



2) Détermination des constantes

• Potentiel standard  $Zn^{2+}/Zn(s)$

$Zn^{2+} + 2e^- = Zn(s)$   $E = E^0 + \frac{0,06}{2} \log [Zn^{2+}]$

à pH = 0  $E = -0,82 = E^0 + 0,03 \log C_{Zn^{2+}}$   $E^0 = E - 0,03 \log C_T$

$\Rightarrow E^0_{Zn^{2+}/Zn(s)} = -0,82 - 0,03 \log(10^{-2})$   $E^0 = -0,75V$

• Produit de solubilité

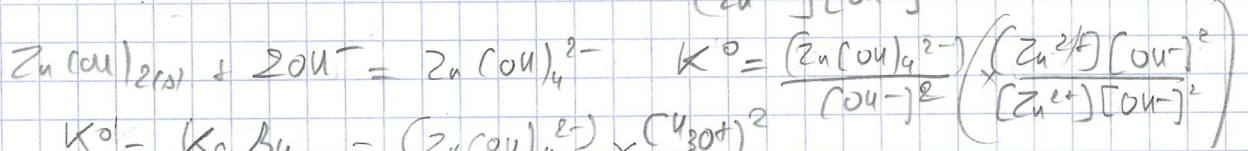
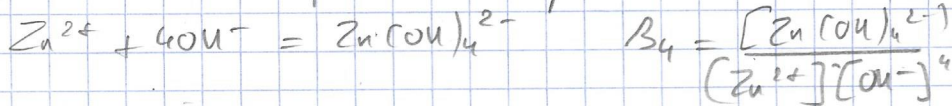
Apparition du précipité pour pH = 6,5  $K_S = [Zn^{2+}][OH^-]^2$

$[OH^-] = \frac{K_e}{h}$   $K_S = C_{Zn^{2+}} \times 10^{-14 \times 2} = C_{Zn^{2+}} \times 10^{-28 + 2pH} = C_{Zn^{2+}} \times 10^{\frac{-15}{13-28}}$

$K_S = 10^{-2} \times 10^{-15} = 10^{-17}$   $pK_S = 17$

$K_S = [Zn^{2+}] \times \frac{K_e^2}{(H_3O^+)^2}$

2) Constante de l'équilibre de complexation  $\beta_4$



$$K^0 = K_s \beta_4 = \frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{Zn}^{2+}]} \times \frac{[\text{OH}^-]^2}{[\text{OH}^-]^2}$$

À la limite de saturation du complexe  $K^0 = K_s \beta_4 = \frac{C_{\text{max}}}{K_e} 10^{-\text{pH} \times 2} \Rightarrow \beta_4 =$

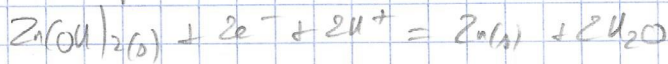
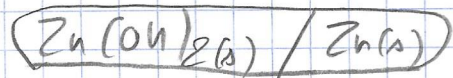
$$K^0 = K_s \beta_4 = C_{\text{max}} \times 10^{28 - 2\text{pH}}$$

$$K^0 = 10^{-2} \times 10^{(28 - 2 \times 13,75)} = 10^{-2 + 0,5} = 10^{-1,5}$$

$$\beta_4 = \frac{K^0}{K_s} = \frac{10^{-1,5}}{10^{-17}} = 10^{17 - 1,5} = 10^{15,5} \quad \left| \log \beta_4 = 15,5 \right|$$

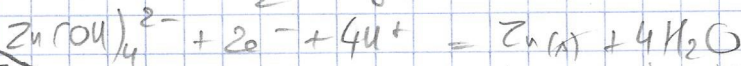
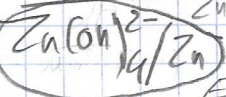
3) Vérification des pentes

C/A



$$E = E^0 + \frac{0,06}{2} \log [\text{H}^+]^2 = E^0 - 0,06 \text{pH} \quad \left| \text{Pente } -0,06 \text{ V} \right|$$

D/A



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

$$E = E^{0''} + \frac{0,06}{2} \log (c_T) - 0,06 \times 2 \log [\text{H}_3\text{O}^+]$$

$$\left| \text{Pente } -0,12 \text{ V} \right|$$

Remarque : Valeur des potentiels standard modifiés

•  $Zn(OH)_2(s) / Zn(s)$

$$E^{10} = E + 0,06 pH$$

Par  $pH = 6,5, E = -0,82V \Rightarrow E^{10} = -0,82 + 0,06 \times 6,5$

$$E^{10} = -0,43V$$

- Veif:  $Zn^{2+} / Zn(s) \quad E = E^0 + \frac{0,06}{2} \lg [Zn^{2+}]$

Or  $K_s = [Zn^{2+}][OH^-]^2 \Rightarrow E = E^0 + \frac{0,06}{2} \lg \frac{K_s}{[OH^-]^2}$

$$E = E^0 + \frac{0,06}{2} \lg \left( \frac{K_s}{K_w^2} \times h^2 \right) = E^0 + \frac{0,06}{2} \lg \frac{K_s}{K_w^2} - 0,06 pH$$

Par identification  $E^{10} = E^0 - \frac{0,06}{2} pH + 0,06 pH$

$$E^{10} = -0,76 - 0,03 \times 17 + 0,06 \times 14 \quad \boxed{E^{10} = -0,43V}$$

•  $Zn(OH)_4^{2-} / Zn(s)$

$$E^{10} = E + 0,12 \lg [H^+] - 0,03 \lg c_{hydr}$$

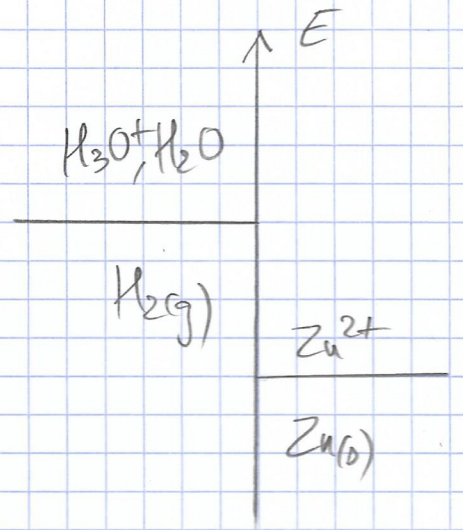
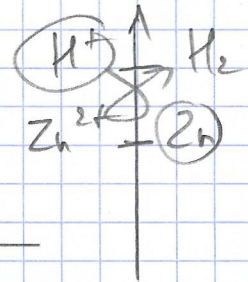
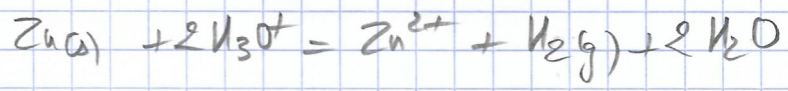
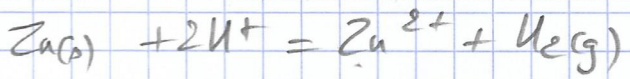
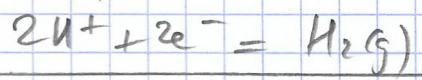
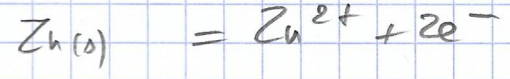
$$= E - 0,12 pH - 0,03 \lg c_{hydr}$$

On n'a pas la valeur  $(E, pH)$  pour calculer  $E^{10}$

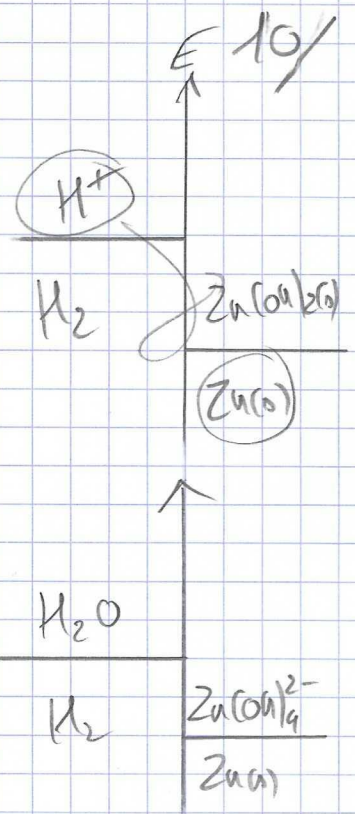
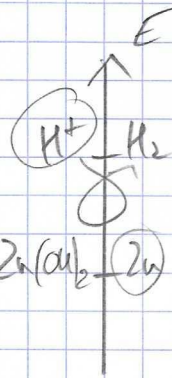
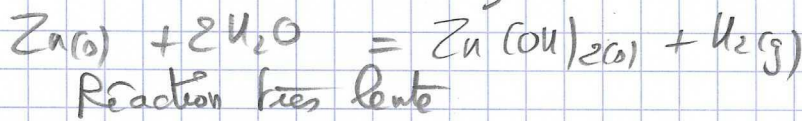
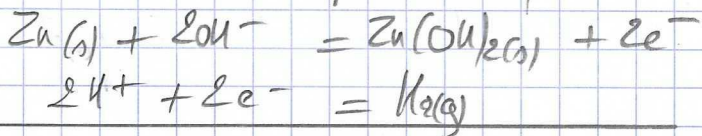
4) Utilisation du diagramme

Le diagramme de prédominance de  $Zn(s)$  est disjoint de celui de l'eau  $\rightarrow Zn(s)$  est donc instable dans l'eau

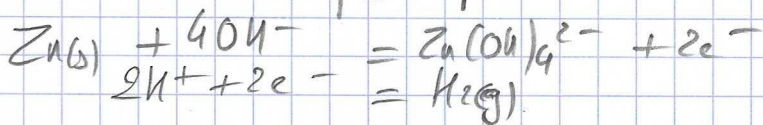
En milieu acide  $pH < 6,5$



En milieu neutre-basique  $6,9 < \text{pH} < 13,75$



En milieu très basique  $\text{pH} > 13,75$



- Le zinc est attaqué par les acides et les bases
- Il subit la corrosion en milieu acide
  - En milieu neutre-basique, il est passivé par une couche d'hydroxyde de zinc  $\text{Zn(OH)}_2\text{(s)}$ .