

Ex II

H.C $\begin{cases} d_1 = a \\ d_2 = \sqrt{\frac{a^2}{3} + \frac{c^2}{4}} \end{cases}$

$T_i \alpha : H.C \begin{cases} c = 468 \text{ pm} \\ a_\alpha = 295 \text{ pm} \\ R_\alpha = \frac{d_2}{2} = 144,7 \text{ pm} \end{cases}$

II $T_i \beta$: système cubique

Hexagonal:
 $2R = \inf(d_1, d_2)$

$R_\beta = \frac{Z \cdot M_{T_i}}{N_A a_\beta^3}$

① Pour la famille (110), $\theta_{(110)} = 19,14^\circ$

Loi de Bragg: $2d_{hkl} \sin \theta = n \lambda$

diffraction du 1^{er} ordre: $n=1$

$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$2 \frac{a_\beta}{\sqrt{h^2 + k^2 + l^2}} \sin \theta = \lambda$

$a_\beta = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$

AN: $a_\beta = \frac{154 \sqrt{2}}{2 \sin(19,14^\circ)} = 332 \text{ pm}$

② $R_\beta = \frac{Z M_{T_i}}{N_A a_\beta^3}$

$Z = \frac{R_\beta N_A a_\beta^3}{M_{T_i}}$

AN: $Z = \frac{4,35 (332 \cdot 10^{-10})^3 \times 6,023 \cdot 10^{23}}{47,9}$

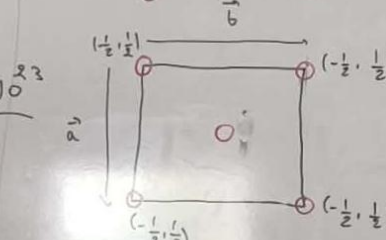
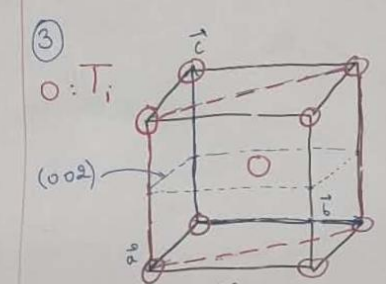
$Z=2$

$\Rightarrow$ mode I

translations permises: $\begin{cases} u\vec{a} + v\vec{b} + w\vec{c} \\ (\frac{u+v+w}{2}) \end{cases}$

$R_q: \rho = \frac{Z M}{N_A V_{maille}} = \frac{M}{V_m}$

$Z = \frac{N_A V_{maille}}{V_m}$

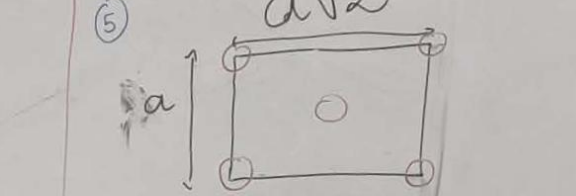


$C = \frac{Z \cdot \frac{4}{3} \pi \cdot R_p^3}{V_m} = 0,68 < 0,74$

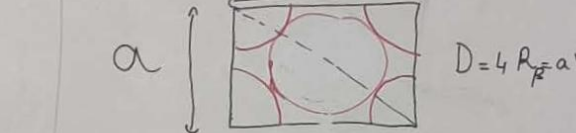
$N_c \nearrow$ le rayon $\nearrow$

$\rightarrow$ n'est pas compact

④ $N_c(T_i) = 8$



R_q : trace avec contact: $a\sqrt{2}$



⑥ Contact des atomes selon la grande diagonale

$4R_p = a\sqrt{3} \Rightarrow R_p = \frac{a\sqrt{3}}{4}$

AN: $R_p = 143,7 \text{ pm} = 1,437 \text{ \AA}$

$R_p < R_\alpha$ en effet $N_c = 12 > N_{c,p} = 8$

Partie B

1) TiN (III)

n.o(Ti) = +III
 $\Rightarrow$ Cation Ti^{3+}

Créat. TiN : (Ti^{3+}, N^{3-})

$p-q=0$ donc $q=p=3$

$\Rightarrow TiN: (Ti^{3+}, N^{3-})$

2) Anion N^{3-} : arrangement C.F.C
 (Somets et centres des faces).

Cation Ti^{3+} : Niveaux des anions et centres des cubes (i.e.) occupent la totalité des S.O du réseau (N^{3-})

$\Rightarrow$ il s'agit d'un structure Type NaCl (6/6)

Condition de stabilité

Catet catan-anion
 $r_+ + r_- = \frac{a}{2}$

non contact anion-anion
 $2r_- \leq \frac{a\sqrt{2}}{2}$

$\Rightarrow r_- < \frac{r_+}{\sqrt{2}} < \frac{\sqrt{3}-1}{2} r_+$

4) $Z(Ti^{3+}) = 1 \times 1 + 12 \times \frac{1}{4} = 4$

$Z(N^{3-}) = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

pour vallo ($4Ti^{3+}, 4N^{3-}$)
 $\Rightarrow 4 TiN \begin{cases} g.f.: TiN \\ n(g.f.) = 4 \end{cases}$

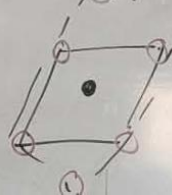
$Ti^{3+}: (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); (\frac{1}{2}, 0, 0); (\frac{1}{2}, 0, 1); (0, 0, \frac{1}{2})$

$N^{3-}: (0, 0, 0); (\frac{1}{2}, \frac{1}{2}, 0); (\frac{1}{2}, 0, \frac{1}{2}); (0, \frac{1}{2}, \frac{1}{2})$

5) TiN de Type NaCl: 6/6

$N_c(Ti^{3+}) = 6$
 $N_c(N^{3-}) = 6$

polyèdre de coordination octaèdre



Catet catan-anion:

$$r_{Ti^{3+}} + r_{N^{3-}} = \frac{a}{2}$$

$$a = 2(r_{Ti^{3+}} + r_{N^{3-}})$$

$$a = 430 \text{ pm} = 4.30 \text{ \AA}$$

$$\rho = \frac{n(g.f.) \cdot M(g.f.)}{N_A \cdot V_{\text{cell}}} = \frac{4 \cdot M_{TiN}}{N_A \cdot a^3}$$

$$a' = \sqrt[3]{\frac{4 \cdot M_{TiN}}{N_A \cdot \rho}} = \sqrt[3]{\frac{4(47.9 + 14)}{6.02 \times 10^{23} (7.84)}}$$

$$a' = 428 \text{ pm} < a = 430 \text{ pm}$$

$\Rightarrow$ la liaison $Ti-N$ est par à 100% ionique

$\Rightarrow$ % C.I. 100%
 % C.C. 0%

Partie D Ge: Cristal covalent

Ge: structure diamant

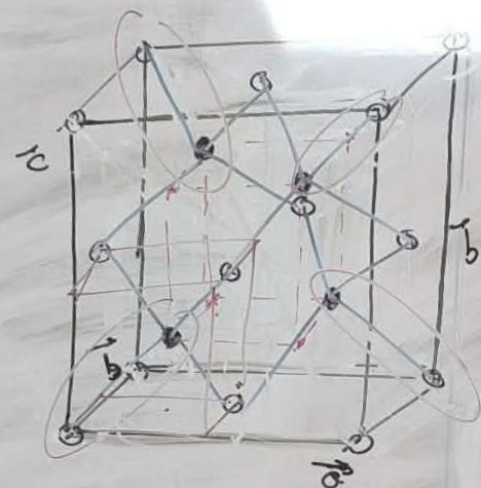
1) Les atomes Ge occupent:

- + Sommets + Centres des faces (C.F.C)
- + la moitié des T alternés.

$Z = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1 = 8$

$(0,0,0) (\frac{1}{2}, \frac{1}{2}, 0) (\frac{1}{2}, 0, \frac{1}{2}) (0, \frac{1}{2}, \frac{1}{2})$

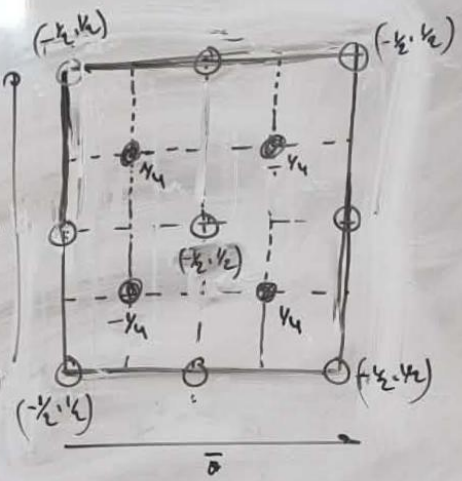
$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}) (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}) (\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$



: liaisons covalentes Ge-Ge

le motif est carré, triègre

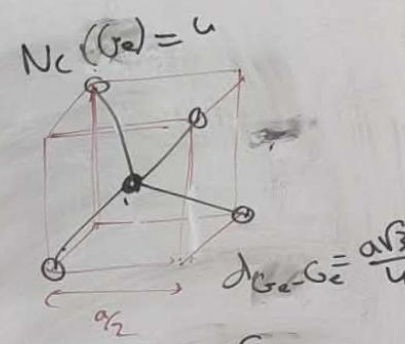
2 atomes de Ge $\begin{cases} (0,0,0) \\ (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \end{cases}$



$Z(\text{Ge}) = 8$: 8 atomes (Ge) par maille

$\Rightarrow 8 \text{ g.f.}(\text{Ge}) \text{ par maille}$

$4 (\text{Ge}-\text{Ge})$: 4 motifs par maille



$N_c(\text{Ge}) = 4$

$d_{\text{Ge-Ge}} = \frac{a\sqrt{3}}{4}$

$Z R_{\text{Ge}} = \frac{a\sqrt{3}}{4}$

$R_{\text{Ge}} = \frac{a\sqrt{3}}{8} = 122,5 \text{ pm}$

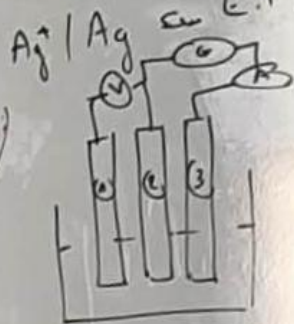
$\rho = \frac{Z \times \frac{4}{3} \pi R_{\text{Ge}}^3}{a^3}$

$\rho = \frac{8 \times \frac{4}{3} \pi (122,5)^3}{(566)^3}$

$\rho = 0,34$

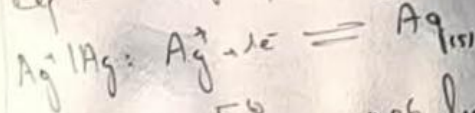
Ex 1 2022/2023 (IPEIS)

E.T (Ag): $i = f(E \text{ V.E.S.H})$



(2/a) allure de la courbe $i = f(E)$ de
système Ag^+ / Ag sur (Ag): système actif

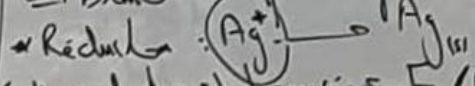
$$E_{eq} = E_{th}(\text{Ag}^+ / \text{Ag}) - E_{ref}$$



$$E_{th}(\text{Ag}^+ / \text{Ag}) = E_{\text{Ag}^+ / \text{Ag}}^0 + \frac{0.06}{1} \log [\text{Ag}^+]$$

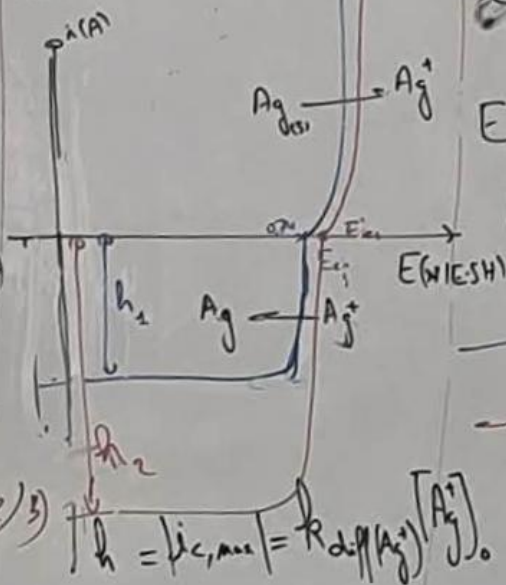
$$E_{th}(\text{Ag}^+ / \text{Ag}) = 0.8 - 0.06 = 0.74 \text{ V.E.S.H}$$

* oxydation: $\text{Ag}_{(s)} \rightarrow \text{Ag}^+$
 (la courbe observée: E) $E_{eq} = 0.74 \text{ V}$
 $\Rightarrow$ branche anodique sans polarisation de diffusion



(la courbe observée: E) ($E_{eq} = 0.74 \text{ V}$)

$\Rightarrow$ branche cathodique avec
 polarisation de diffusion de la réaction
 électroactive (Ag^+): $[\text{Ag}^+]_{0,1}$ faible



$$[\text{Ag}^+]_{0,2} = 0.2 \text{ mol.L}^{-1}$$

hauteur de polarisation dépend $[\text{Ag}^+]_{0,1}$

$$\text{Carne } [\text{Ag}^+]_{0,2} = 2 [\text{Ag}^+]_{0,1}$$

$$\Rightarrow h_2 = 2 h_1$$

$$E_{eq} = E_{\text{Ag}^+ / \text{Ag}}^0 + \frac{0.06}{1} \log [\text{Ag}^+]_{0,2}$$

$$E_{eq} = 0.76 \text{ V.E.S.H}$$

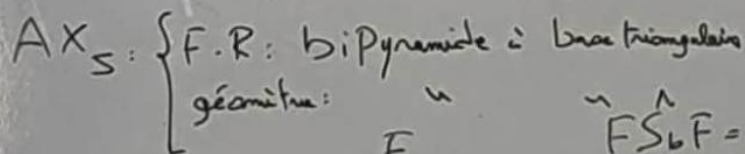
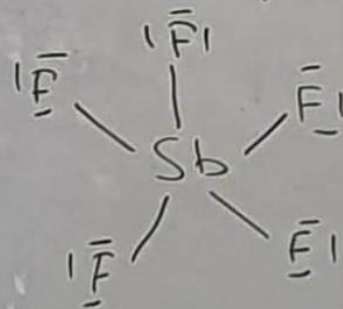
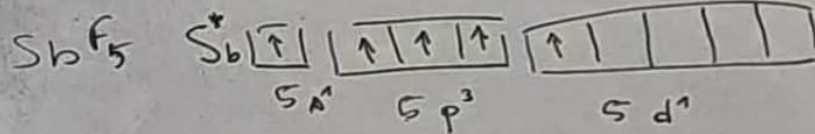
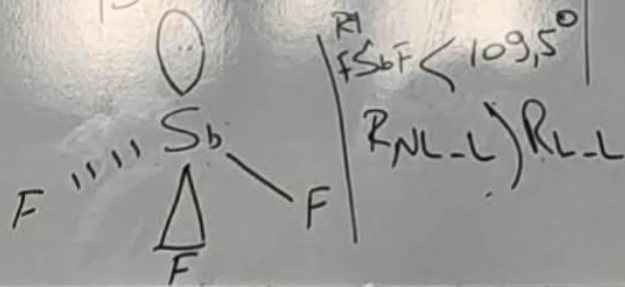
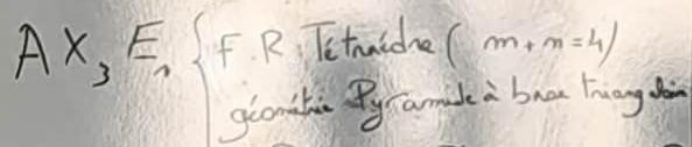
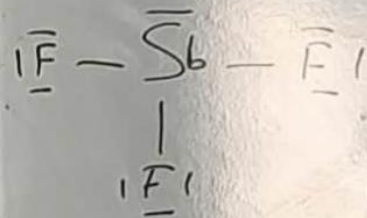
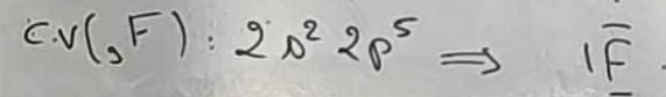
$$[\text{Ag}^+]_{0,1} = 0.1 \text{ mol.L}^{-1}$$

$$[\text{Ag}^+]_{0,2} = 0.2 \text{ mol.L}^{-1}$$

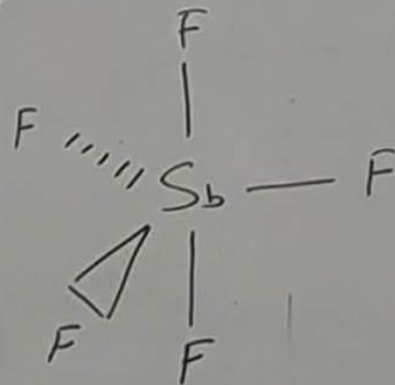
$$h = \frac{i_L}{i} = \frac{R_{diff}(\text{Ag}^+)}{[\text{Ag}^+]_{0,1}}$$

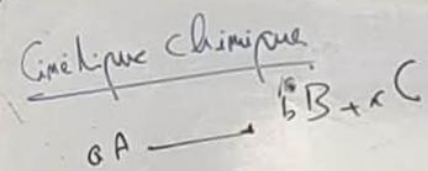
B6

Q6



$\angle F\hat{Sb}F = 90^\circ$
et 120°





La vitesse :

$$V_R = \frac{1}{V} \cdot \frac{d\xi}{dt}$$

$$V_R = k(T) [A]^\alpha = -\frac{1}{a} \frac{d[A]}{dt}$$

1^{er} cas : $\alpha = 0$

$$[A]_t = [A]_0 - a k t : \text{dte}$$

$$k(T) = \frac{[A]_0 - [A]}{a t} : \text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$$

$$\text{à } t_{1/2} : [A]_t = \frac{[A]_0}{2} \Rightarrow t_{1/2} = \frac{[A]_0}{2 a k}$$

1^{re} expérience $[A]_{0,1} (t_{1/2})_1$
 2^{de} expérience $[A]_{0,2} = 2[A]_{0,1}$
 $(t_{1/2})_2 = 2(t_{1/2})_1$

$\Rightarrow t_{1/2}$ est proportionnelle à $[A]_0$

Vitesse initiale ($\alpha = 0$)
 $V_0 = k(T) [A]_0 = k(T)$

V_0 est indépendante de $[A]_0$

2^{de} cas : ($\alpha = 1$)

$$V_R = -\frac{1}{a} \cdot \frac{d[A]}{dt} = k[A]$$

$$\ln[A] = \ln[A]_0 - a k t$$

$$\ln \frac{[A]_0}{[A]} = a k t$$

$$\ln[A]_t = f(t) : \text{dte}$$

$$* k(T) = \frac{\ln \frac{[A]_0}{[A]_t}}{a t}$$

$$k(T) : (t^{-1})$$

$$\text{à } t_{1/2} : [A] = \frac{[A]_0}{2}$$

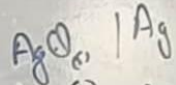
$$t_{1/2} = \frac{\ln 2}{a k}$$

$t_{1/2}$: indépendant de $[A]_0$

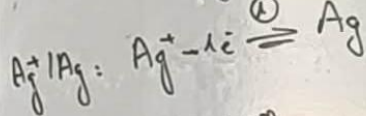
* Vitesse initiale
 $V_0 = k[A]_0$
 1^{re} expérience : $[A]_{0,1}$
 $V_{0,1} = k(T) [A]_{0,1}$
 2^{de} expérience : $[A]_{0,2} = 2[A]_{0,1}$
 $V_{0,2} = k[A]_{0,2} = 2k[A]_{0,1}$
 $\Rightarrow V_{0,2} = 2V_{0,1}$
 $\Rightarrow V_0$ est proportionnelle à $[A]_0$

Ex 1 2022/2023 (IPEIS)

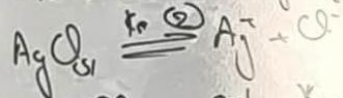
c) I/O: Ag^+ / Ag



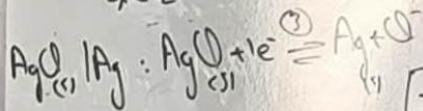
① Ag



$\Delta_r G_1^\circ = -F E^\circ_{Ag^+ / Ag}$



$\Delta_r G_2^\circ = -RT \ln K_s$



$\Delta_r G_3^\circ = -F E^\circ_{AgCl / Ag}$

③ = ① + ②

$\Delta_r G_3^\circ = \Delta_r G_1^\circ + \Delta_r G_2^\circ$

$-F E^\circ_{AgCl / Ag} = -F E^\circ_{Ag^+ / Ag} - RT \ln K_s$

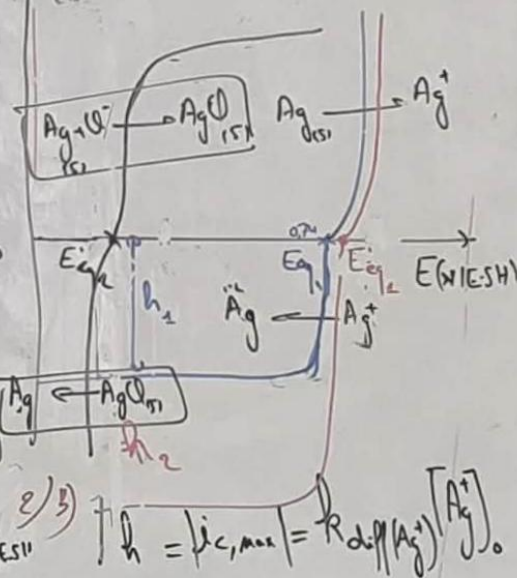
$E^\circ_{AgCl / Ag} = E^\circ_{Ag^+ / Ag} + \frac{RT}{F} \ln K_s$

$E^\circ_{AgCl / Ag} = E^\circ_{Ag^+ / Ag} + 0,06 \log K_s$

AN: $E^\circ_{AgCl / Ag} = 0,8 + 0,06 \log 10^{-10}$
 $= 0,2 \text{ (N.I.E.S.H.)}$

$E_{R(AgCl / Ag)} = E^\circ_{AgCl / Ag} + 0,06 \log \frac{1}{[Cl^-]}$

$E_{R(AgCl / Ag)} = 0,2 + 0,06 = 0,26 \text{ V (N.I.E.S.H.)}$



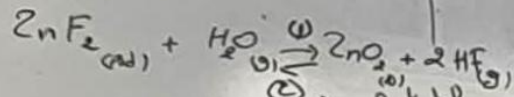
c) sys $AgCl / Ag$ sur Ag
 oxydation: $Ag + Cl^- \rightarrow AgCl_{(s)} + e^-$

ceux observés sont:
 $E > E_{eq} \Rightarrow$ branche anodique avec polarisation de diffusion (Cl^- : espèce électroactive)
 $[Cl^-]_0 = 0,1 \text{ mol/l}$

réduction: $AgCl_{(s)} + e^- \rightarrow Ag + Cl^-$
 cath. réduction observée $E < E_{eq}$

$\Rightarrow$ branche cathodique sur polarisation de diffusion: espèce électroactive ($AgCl_{(s)}$): fixe sur électrode (Ag)

Concours PC 2012 | $P_i = T_i P$



1^{ère} méthode : Aspect qualitatif
(Loi de Le Chatelier)

un ↑ de P à $T = \text{cte}$ déplace
le sys dans le sens qui fait diminuer $n(g)$
(c-à-d du sens inverse (2))

$$Dm(g) = (2-1) = +1 \begin{cases} \text{sens direct } m(g) \\ \text{se inverse } m(g) \end{cases}$$

2^{ème} méthode : Aspect qualitatif

$$D_n G(T) = D_n G^0 + RT \ln Q$$

$$D_n G(T) = RT \ln \frac{Q(T)}{K^0(T)}$$

$$Q(T) = \frac{P_{HF}^2}{P_{H_2O}} \cdot \frac{1}{P^0}$$

$$Q(T) = \frac{\gamma_{HF}^2}{\gamma_{H_2O}} \cdot \left(\frac{P}{P^0} \right)$$

$$\Rightarrow P \uparrow \quad Q(T) \uparrow$$

$$\text{de } Q \rightarrow K^0(T)$$

$\Delta G(T) = 0$: le sys se déplace
dans le sens inverse

$$P_i = \frac{P_i}{P} \cdot RT = [i] RT$$

ajout de gaz inertes à $T = \text{cte}$ $P = \text{cte}$
 $\forall \uparrow Q(T) \Rightarrow Q(T) < K^0(T)$
($\Rightarrow$ le sys évolue de le sens direct)

1) Influence de la pression addition de $ZnF_{2(s)}$
 $ZnF_{2(s)}$: catalyseur inactif car n'intervient pas
dans la loi d'action de masse
 $\Rightarrow$ le sys reste en équilibre

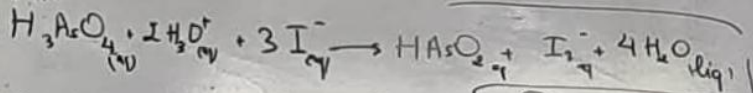
2) addition de gaz inerte
i) à $T = \text{cte}$ et $V = \text{cte}$: le sys évolue par
c-à-d le sys reste en équilibre
ii) à $T = \text{cte}$ et $P = \text{cte}$:
le sys évolue de le sens d'augmenter $n(g)$ (c-à-d
de le sens direct)

$$D_n G(T) = RT \ln \frac{Q(T)}{K^0(T)} = \frac{P_{HF}^2}{P_{H_2O}} \cdot \frac{1}{P^0} = \frac{P_{HF}^2}{P_{H_2O}} \cdot \left(\frac{RT}{V P^0} \right)$$

$$Q(T) = K^0(T) \Rightarrow \text{le sys reste en équilibre}$$

B6 2023

Pro II



$$V = k(T) \cdot [H_3AsO_4]^\alpha \cdot [H_3O^+]^\beta \cdot [I^-]^\gamma$$

avec α : l'ordre partiel r. H_3AsO_4

β : l'ordre partiel r. H_3O^+

γ : l'ordre partiel r. I^-

$k(T)$: cte de vitesse

Rq:

$$k(T) = A_0 \exp\left(-\frac{E_a}{RT}\right)$$

E_a : énergie d'activation

exp 1:

γ : ?

expression 1:

$$V_{0,1} = k(T) \cdot [H_3AsO_4]_{0,1}^\alpha \cdot [H_3O^+]_{0,1}^\beta \cdot [I^-]_{0,1}^\gamma$$

exp 2:

$$V_{0,2} = k(T) \cdot [H_3AsO_4]_{0,2}^\alpha \cdot [H_3O^+]_{0,2}^\beta \cdot [I^-]_{0,2}^\gamma$$

$$\alpha [H_3AsO_4]_{0,2} = [H_3AsO_4]_{0,1}$$

$$\text{et } [H_3O^+]_{0,2} = [H_3O^+]_{0,1}$$

$$\frac{V_{0,2}}{V_{0,1}} = \left(\frac{[I^-]_{0,2}}{[I^-]_{0,1}} \right)^\gamma$$

$$2^1 = \left(\frac{0,2}{0,1} \right)^\gamma = 2^\gamma$$

$$\Rightarrow \gamma = 1$$

β : ?

exp 3:

$$V_{0,3} = k(T) [H_3AsO_4]_{0,3}^\alpha [H_3O^+]_{0,3}^\beta [I^-]_{0,3}^\gamma$$

exp 4:

$$V_{0,4} = k(T) [H_3AsO_4]_{0,4}^\alpha [H_3O^+]_{0,4}^\beta [I^-]_{0,4}^\gamma$$

or $[H_3AsO_4]_{0,4} = [H_3AsO_4]_{0,3}$

$$\frac{V_{0,3}}{V_{0,4}} = \left(\frac{[H_3O^+]_{0,3}}{[H_3O^+]_{0,4}} \right)^\beta \frac{[I^-]_{0,3}}{[I^-]_{0,4}}$$

$$2^1 = \left(\frac{10 \cdot 10^{-3}}{5 \times 10^{-3}} \right)^\beta \left(\frac{0,1}{0,2} \right)^1$$

$$2^1 = (2)^\beta \cdot \frac{1}{2}$$

$$2^2 = 2^\beta \Rightarrow \beta = 2$$

exp 2

$$V_{0,1} = [H_3AsO_4]_{0,1}^\alpha [H_3O^+]_{0,1}^\beta [I^-]_{0,1}^\gamma$$

exp 3

$$V_{0,3} = [H_3AsO_4]_{0,3}^\alpha [H_3O^+]_{0,3}^\beta [I^-]_{0,3}^\gamma$$

$$\frac{V_{0,3}}{V_{0,1}} = \left(\frac{[H_3AsO_4]_{0,3}}{[H_3AsO_4]_{0,1}} \right)^\alpha$$

$$2^1 = 2^\alpha$$

$$\Rightarrow \alpha = 1$$

l'ordre globale:

$$\alpha + \beta + \gamma = 1 + 2 + 1 = 4$$

$(\alpha + \beta + \gamma) \neq \sum \nu_i$

donc la R° n'est pas élémentaire