

Partie C : Electrochimie

Chap I - Diagramme E-pH
(diagramme Pourbaix)

Diagramme E-pH

* de frontière OX / Red

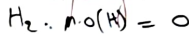
* de frontière Acide / Base

$$\begin{aligned} \chi(F) &= 4 \\ \chi(O) &= 3,7 \\ \chi(C) &= 2,4 \\ \chi(H) &= 2,2 \end{aligned}$$

Couple OX / Red : le nombre d'oxydation (n.o.)
Change : Transfert d'e

Couple acide / base : le nombre d'oxydation (n.o.)
Se conserve : Transfert (H⁺)

hydrogène

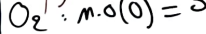


hydrogène métallique : n(H)

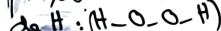
$$\Rightarrow n.o(H) = -I$$

les autres composés : n.o(H) = +I

oxygène



peroxyde : n.o(O) = -I

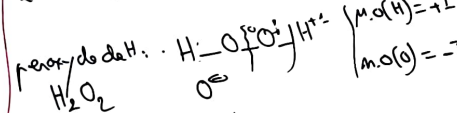
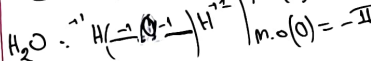
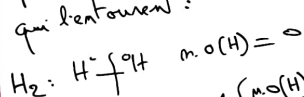


les autres composés : n.o(O) = -II

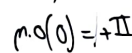
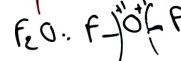
nombre d'oxydation : n.o.

(-s) la charge portée par l'élément (M)

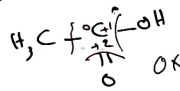
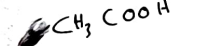
après rupture fictive des liaisons qui l'entourent :



exceptions (O)



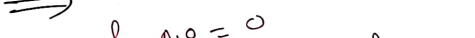
acide éthanoïque



$$n.o(C) = +III$$

* Dans la forme OX ; l'élément possède le n.o le plus élevée

* Dans la forme Red ; l'élément possède le n.o le plus faible



Couple Simple : n.o = 0

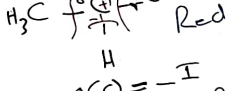
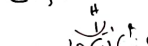
* couple Simple : n.o : charge portée par l'ion



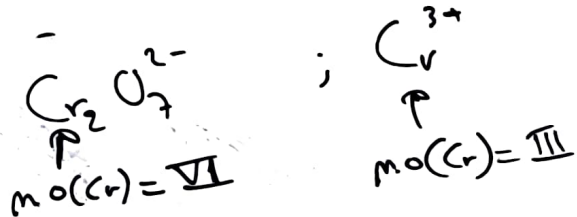
* groupement polyatomique

$$\sum n.o = \text{charge totale}$$

éthanol

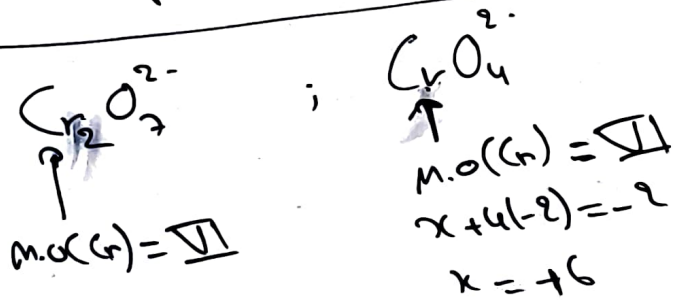
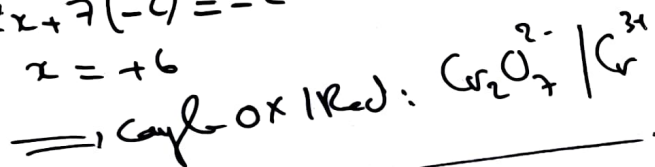


$$n.o(O) = -II$$



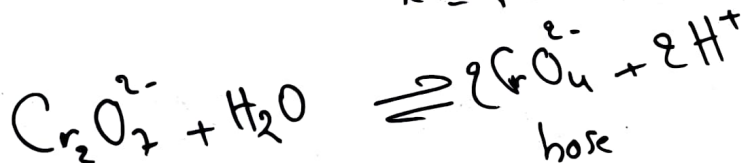
$$2x + 7(-2) = -2$$

$$x = +6$$

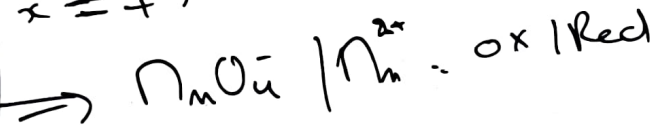
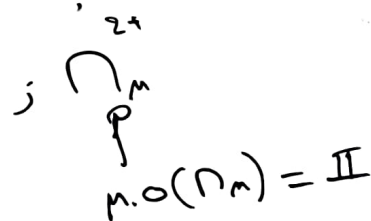
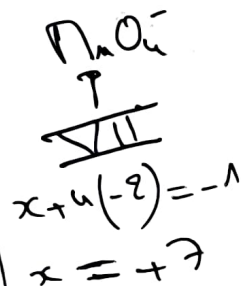
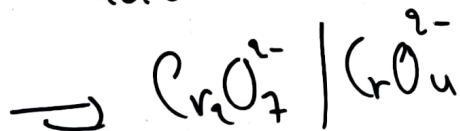


$$x + 4(-2) = -2$$

$$x = +6$$



acids



Part C: Electrochemistry $T = 298\text{K}$

Chap I - Diagramme E-pH (diagramme Pourbaix) (°: 17)

Dimer-reaction of 1 Red

Demi-réaction OX/Red:

$$\alpha \text{ OX} + m\text{e}^- + n\text{H}^+ \rightleftharpoons \beta \text{ Red} + y \text{ H}_2\text{O}$$

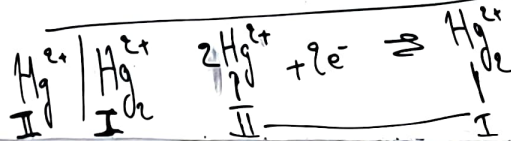
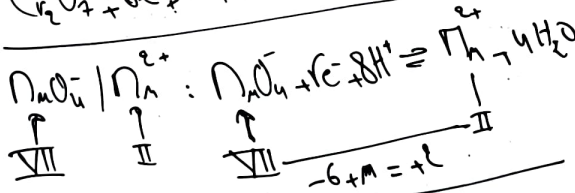
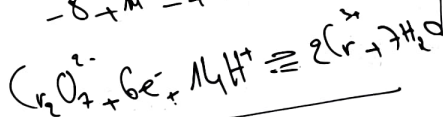
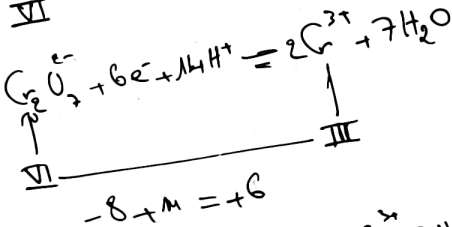
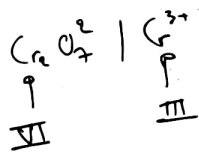
de l'élément dans le 2^e état

et déterminer les n.º de réactif
élément : α et β

- Conservation de l'énergie : ΔE
- déterminer $m_b(e^-)$: m : différence de m.o par atome

- * Conservation de la charge en utilisant $H^+ \rightarrow m$

- * Conservação da matéria $\Rightarrow y$
- * Conservação da matéria do O₂ H₂ e utilizando H₂O



aktivte a_i :

(i): espèce aqueuse (dissoute)
ion: $a_i = \frac{[i]}{c_0}$

(i) : espécie na quene (na do xat)

$$(i) \quad a_i = \frac{p_i}{p_0}$$

$$\log_{10} x = \frac{\ln x}{2.3}$$

$F = \text{Jed's Faraday}$

la charge d'1 mole (e^-)

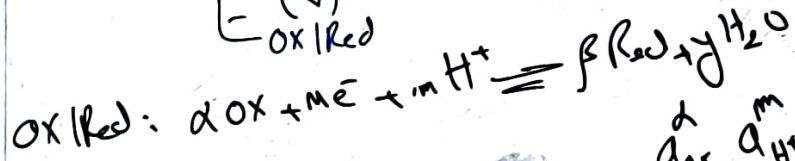
$$F = N_n |e| = 6.083 \times 10^{23} \text{ (1.6/Å)}^{-1}$$

$$F = 96500 \text{ C mol}^{-1}$$

I) date frontière ox/red

Potentiel de Nernst du couple ox/red

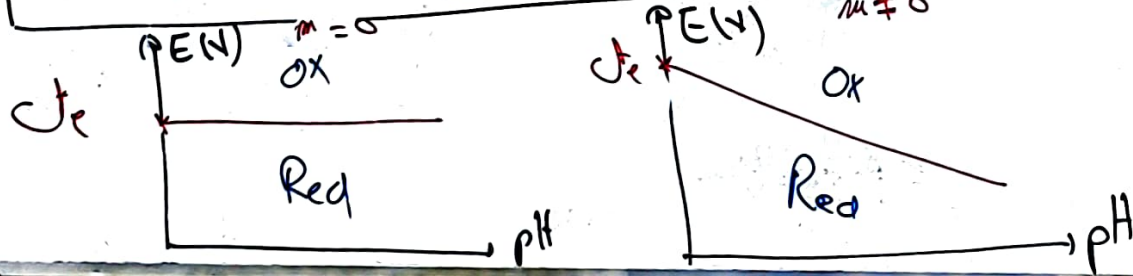
$$E_{ox/red}^{(V)}$$



$$E_{ox/red} = E_{ox/red}^0 + \frac{RT}{nF} \ln \frac{a_{ox}^\alpha a_{H^+}^m}{a_{red}^\beta}$$

$$E_{ox/red} = E_{ox/red}^0 + 2,3 \left(\frac{RT}{nF} \right) \log \frac{a_{ox}^\alpha}{a_{red}^\beta} + \frac{2,3 RT}{F} \left(\frac{m}{n} \right) \log \frac{[H^+]}{C_0}$$

$$E_{ox/red} = E_{ox/red}^0 + \frac{0,06}{n} \log \frac{a_{ox}^\alpha}{a_{red}^\beta} - 0,06 \left(\frac{m}{n} \right) pH$$



$$pH = -\log_{10} [H^+]$$

$$pK_e = -\log_{10} K_0$$

$$pK_s = -\log K_s$$

espèce: aqueuse:

→ domaine de prédominance

espèce non aqueuse
(sol. / liq.)

→ domaine d'existence

Partie C : Electrochimie $T = 298K$
 (Chap I - Diagramme E-pH $C^0 : 1M$)
 (diagramme Pourbaix)

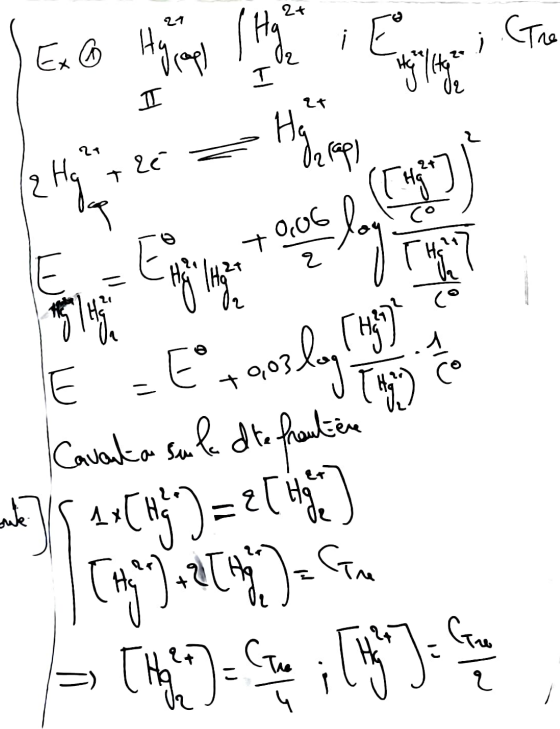
Convention sur la dte frontiere
 Couple (ox)_{aq} / (red)_{aq} : les 2 espèces sont aqueuses.

* Egalite des Concentrations en element atomique
 dans les espèces dissoutes

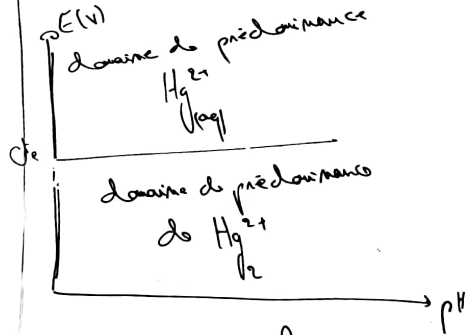
* la somme des concentrations en element atomique
 dans les espèces dissoutes est égale à $C_{T,Hg}$

[element atomique dans l'espèce dissoute] = atomicité (espèce dissoute)

atomicité : nb(atome) par espèce

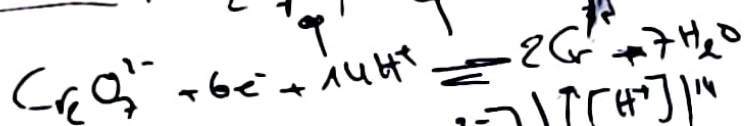
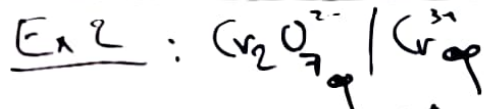


$$E_{Hg^{2+}/Hg^{2+}_2} = E^0_{Hg^{2+}/Hg^{2+}_2} + 0,03 \log \frac{C_{T,Hg}}{C^0}$$



$$E - E^0 = 0,03 \log C_{T,Hg}$$

$$C_{T,Hg} = 10^{\frac{E-E^0}{0,03}}$$



$$E = E^0 + \frac{0.06}{6} \log \frac{\left(\frac{[Cr_2O_7^{2-}]}{C^0}\right) \left(\frac{[H^+]}{C^0}\right)^{14}}{\left(\frac{[Cr^{3+}]}{C^0}\right)^2}$$

$$E = E^0 + 0.01 \log \frac{[Cr_2O_7^{2-}] C^0}{[Cr^{3+}]^2} - 0.14 pH$$

Convention sur la distribution

$$\begin{cases} 2[Cr_2O_7^{2-}] = [Cr^{3+}] \\ 2[Cr_2O_7^{2-}] + [Cr^{3+}] = C_{Tn} \end{cases}$$

$$[Cr_2O_7^{2-}] = \frac{C_{Tn}}{4} ; [Cr^{3+}] = \frac{C_{Tn}}{2}$$

$$E^{(v)} = \frac{E^0 - 0.01 \log C_{Tn} - 0.14 pH}{5e}$$

