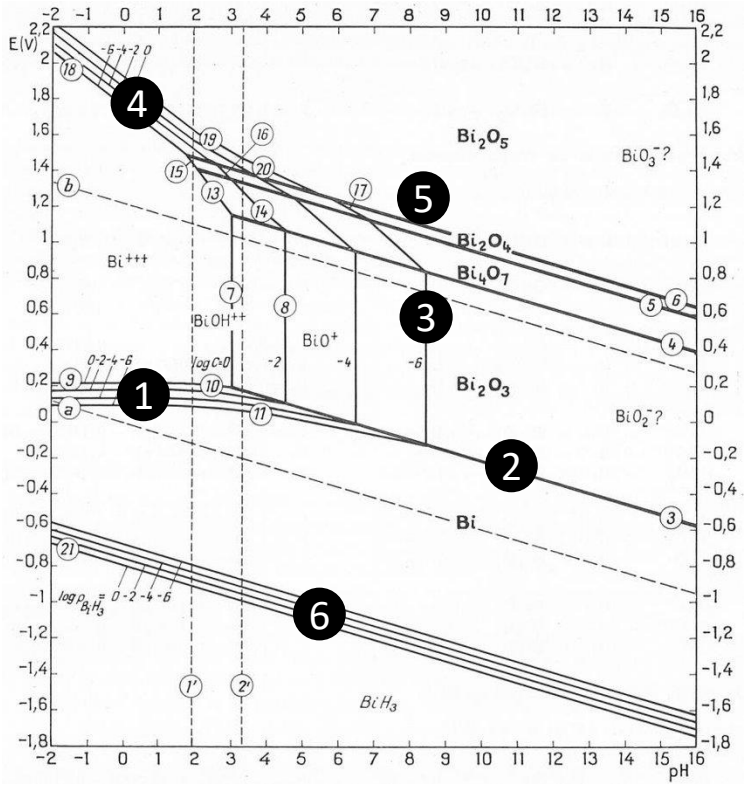
Exercise1: Pourbaix diagram

You want to electrodeposit bismuth from an aqueous electrolyte and you want to choose the ideal conditions.

You decide to refer to the E-pH thermodynamic equilibriums found in Pourbaix diagram.

You find the Pourbaix diagram for Bi^{3+} in pure water at ambient conditions:



1) What represent the vertical, horizontal, and diagonal lines. What are their duplicated lines?
2) What are the diagonal dashed lines? Write the reactions? Name the space defined between them.
3) Write the reactions that occur at the transitions 1, 2, 3, 4, 5, and 6
4) Calculate their slope in the E-pH domain.
5) From the Pourbaix diagram, propose boundary conditions on E, pH and $[Bi^{3+}]$ for the electrodeposition of Bi^0

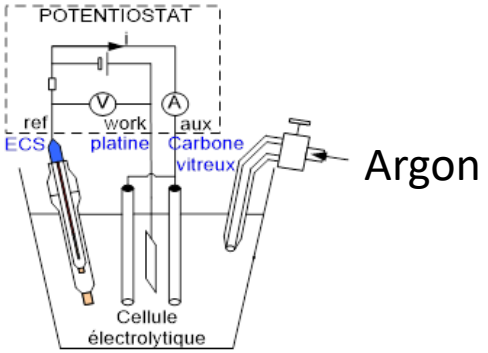
Exercise2: electrodeposition rate and current efficiency

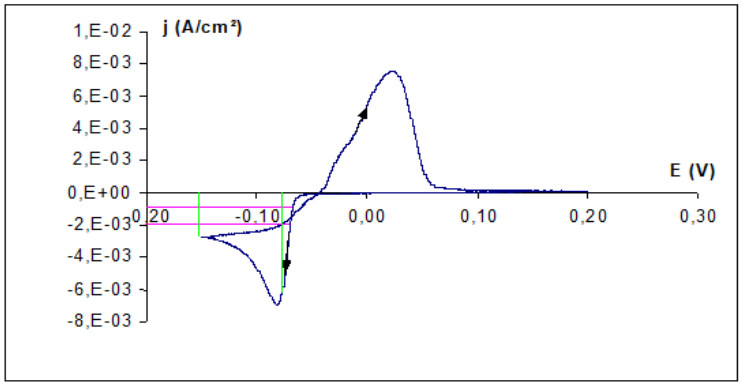
The quantity of reduced cations is linked to the quantity of coulombs by the

Faraday law: $Q = \int i(t)dt = znF$ Quantity of charge (coulomb) ∝ quantity of matter

Faraday constant $F = q\mathcal{N}_A = 96485\ C.mol^{-1}$

Bismuth is electrodeposited from a degased aqueous electrolyte ([Bi^{3+}] = 10^{-2} mol.L^{-1}, [HNO_3] = 1 M) on an 1 cm^2 working electrode at a sufficiently large overpotential





1) Propose a protocole to measure the diffusion coefficient of Bi^{3+}.
2) Knowing that $D_{Bi^{3+}} = 10^{-5}$ $cm^2.s^{-1}$, express the deposition rate of bismuth in $mol.s^{-1}$ as a function of time under purely mass limiting regime and in the absence of convection.
3) Calculate the thickness of the deposit obtained after 1000 s of electroplating (M_{Bi} = 208.98 $g.mol^{-1}$ and ρ_{Bi} = 9.79 $g.cm^{-3}$).
4) After an electrodeposition of 1000 s, a total of 0.4 C was integrated from the chronoamperometry data. Calculate the electrodeposition efficiency.
5) What could have happened to the other electrons? How could you improve the efficiency?
6) What parameters could allow you to tune the growth rate? What could be the trade-offs?