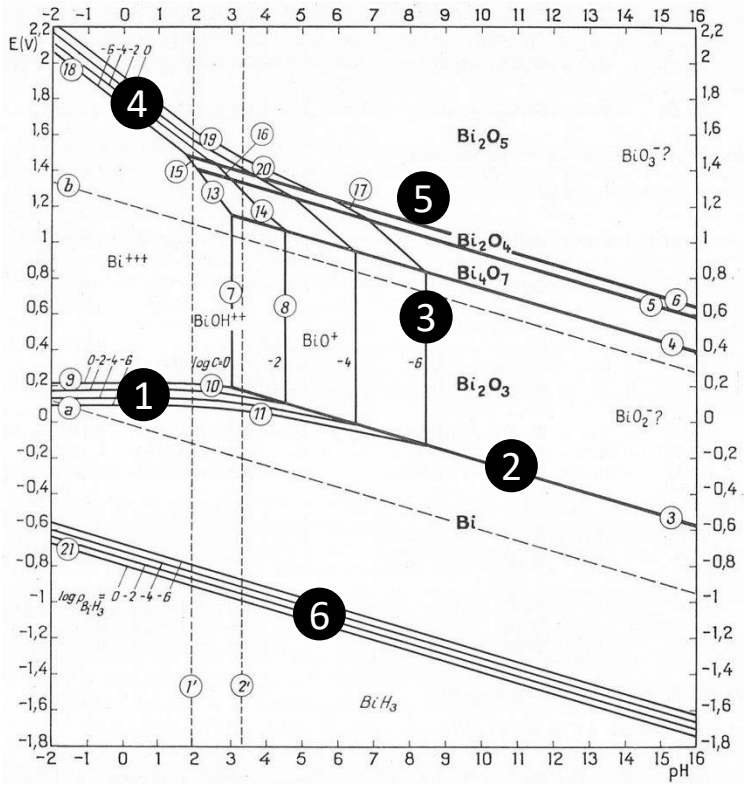
Exercise1: Pourbaix diagram

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

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. Why 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) Determine their slope.
5) From the Pourbaix diagram, propose boundary conditions on E, pH and $[Bi^{3+}]$ for the electrodeposition of Bi^0

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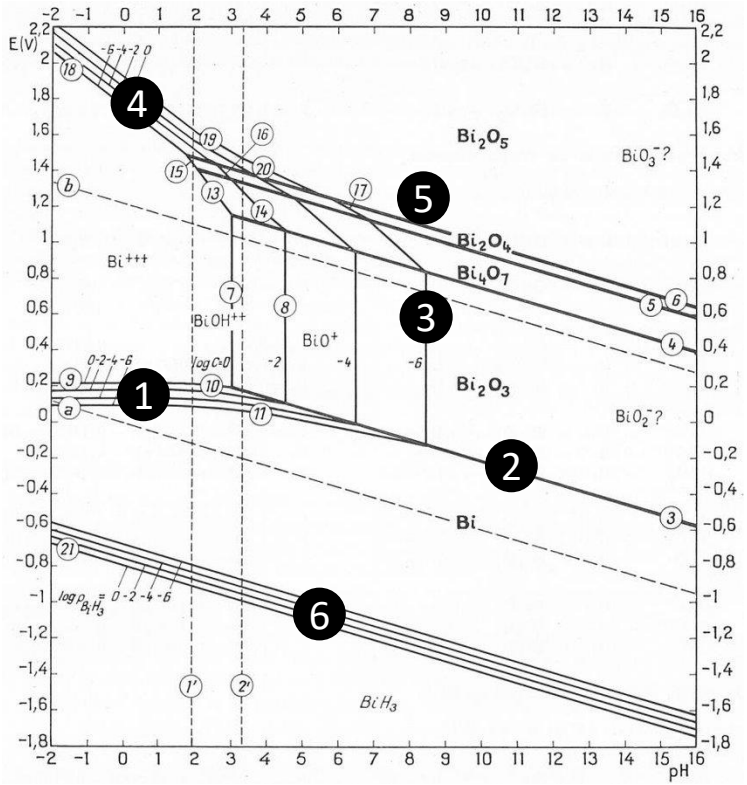

1) What represent the vertical, horizontal, and diagonal lines. Why are their duplicated lines?

Vertical: acid-base reactions which do not depend on the potential without electron transfer

Horizontal: redox reaction which do involve neither H^+ nor OH^-

Diagonal: redox reactions in which hydroxide or hydrogen are involved

Line duplicates show the effect of Bi^{3+} concentration

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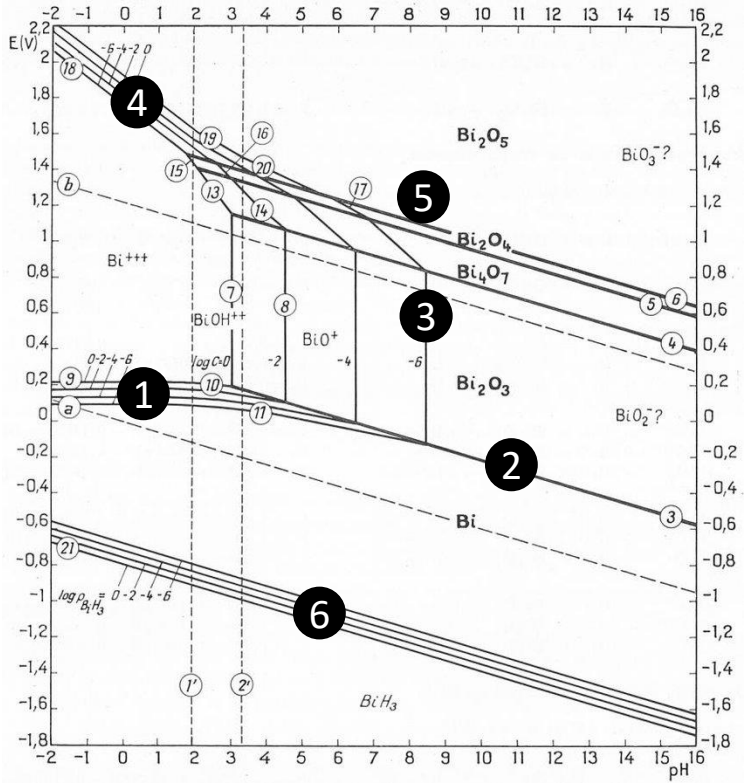

2) What are the diagonal dashed lines? Write the reactions? Name the space defined between them.

The bottom diagonal dashed line represents the equilibrium potential for H_2 evolution

$$2H_3O^+ + 2e^- \rightleftharpoons H_2 + 2H_2O \qquad E^{eq} = E^0_{H^+/H_2} - \frac{RT}{2F} ln \frac{[H^+]^2}{[H_2]} = 0 - 0.059\, pH$$

The top diagonal dashed line represents the equilibrium potential for O_2 evolution

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^{eq} = E^0_{O_2/H_2O} - \frac{RT}{4F} ln \frac{[H^+]^4[O_2]}{[H_2O]^2} = 1.23 - 0.059\, pH$$

The space between is the **electrochemical window** of water where it is neither reduced nor oxidized

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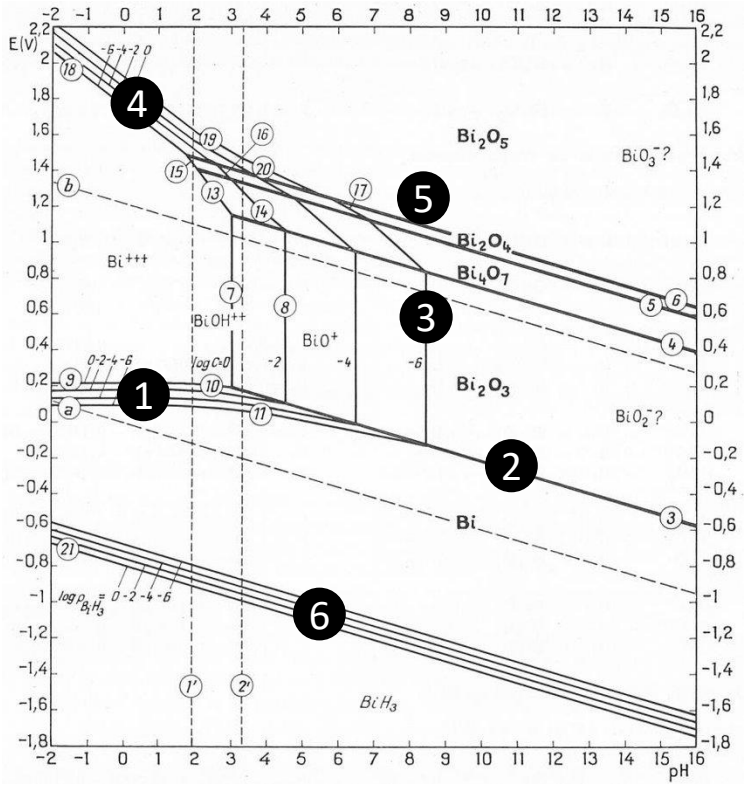

3) Write the reactions that occur at the transitions 1, 2, 3, 4, 5, and 6

(1) $Bi^{3+} + 3e^- \rightleftharpoons Bi^0$

(2) $Bi_2O_3 + 6H^+ + 6e^- \rightleftharpoons Bi^0 + 3H_2O$

(3) $2BiO^+ + H_2O \rightleftharpoons Bi_2O_3 + 2H^+$

(4) $Bi_2O_5 + 4e^- + 10H^+ \rightleftharpoons 2Bi^{3+} + 5H_2O$

(5) $Bi_2O_5 + 2e^- + 2H^+ \rightleftharpoons Bi_2O_4 + H_2O$

(6) $Bi^0 + 3H^+ + 3e^- \rightleftharpoons BiH_3$

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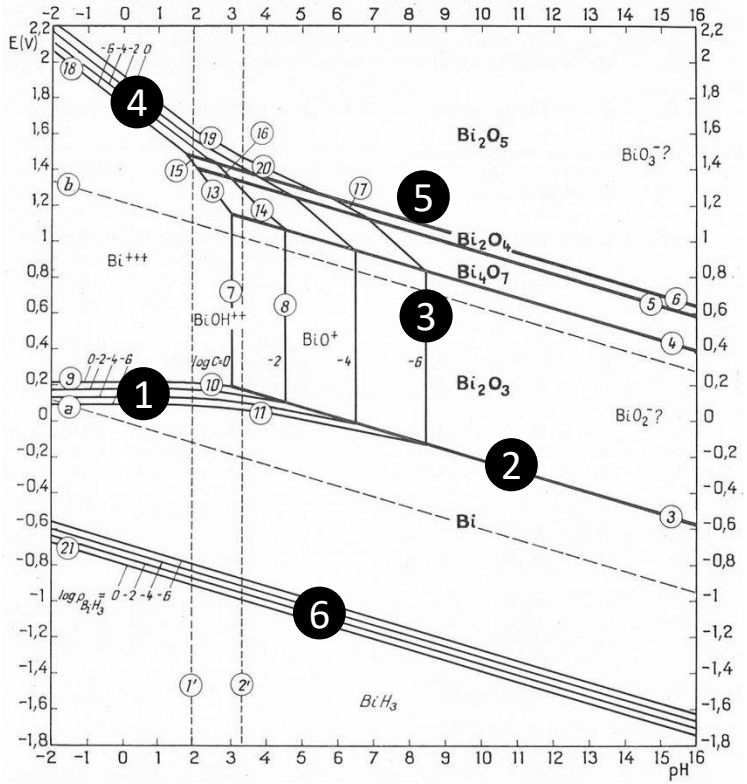


Apply the Nernst equation !!!

The activity of solvents, solids, and gases are taken as 1

4) Determine their slope.

(1) $Bi^{3+} + 3e^- \rightleftharpoons Bi^0$ $\quad E^{eq} = E^0_{Bi^{3+}/Bi} - \frac{RT}{3F} ln \frac{[Bi^{3+}]}{[Bi]} \neq f(pH)$ → horizontal line

(2) $Bi_2O_3 + 6H^+ + 6e^- \rightleftharpoons 2Bi^0 + 3H_2O$ $\quad E^{eq} = E^0_{Bi_2O_3/Bi} - \frac{RT}{6F} ln \frac{[Bi_2O_3][H^+]^6}{[Bi]^2[H_2O]^3}$ → $\propto -0.059\ pH$

(3) $2BiO^+ + H_2O \rightleftharpoons Bi_2O_3 + 2H^+$ $\quad$ no electron exchanged: $\frac{RT}{zF} \mapsto \infty$ → vertical line

(4) $Bi_2O_5 + 4e^- + 10H^+ \rightleftharpoons 2Bi^{3+} + 5H_2O$ $\quad E^{eq} = E^0_{Bi_2O_5/Bi^{3+}} - \frac{RT}{4F} ln \frac{[Bi_2O_5][H^+]^{10}}{[Bi^{3+}]^2[H_2O]^3}$ → $\propto -\frac{10}{4} \cdot 0.059\ pH$

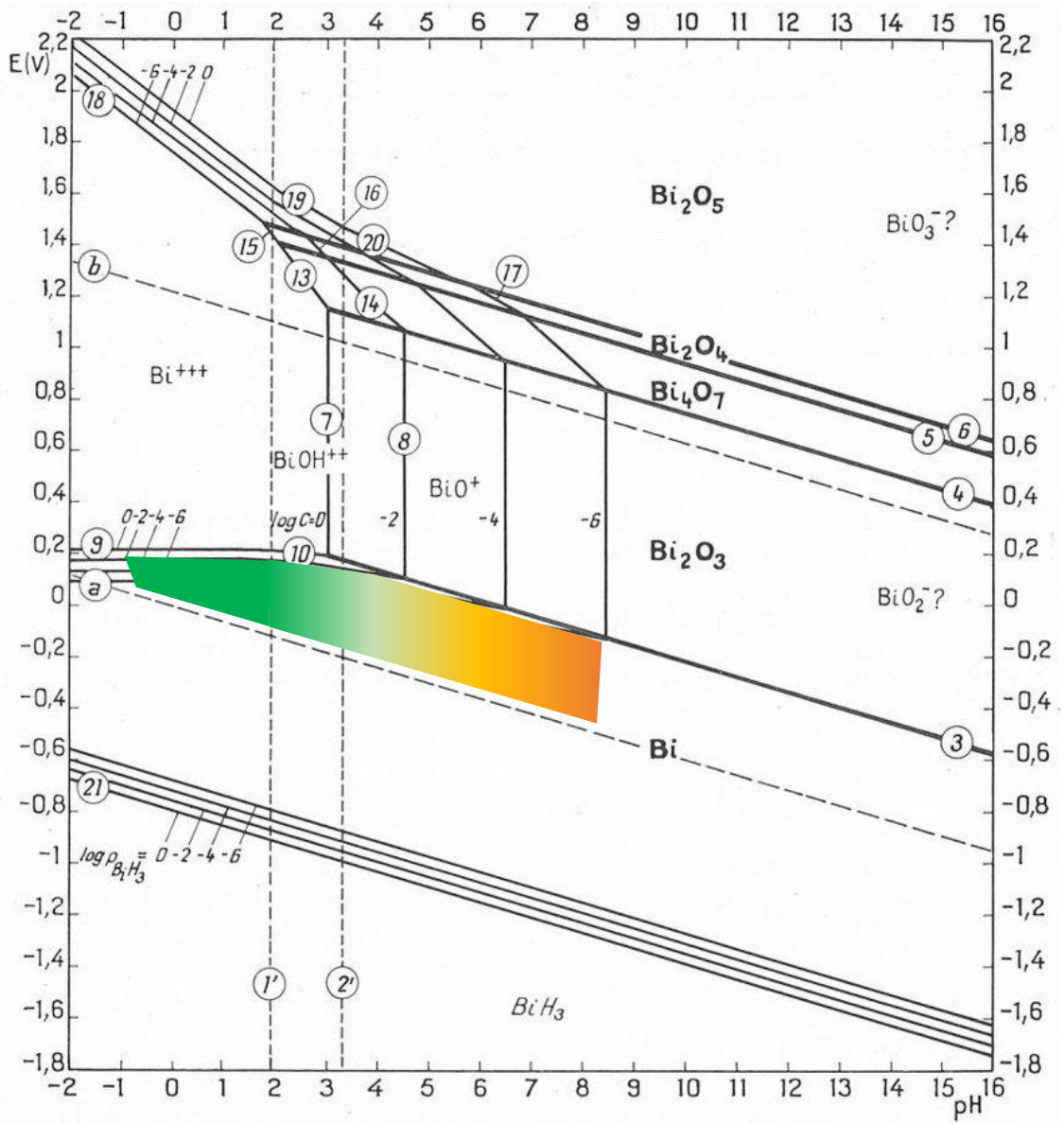
(5) $Bi_2O_5 + 2e^- + 2H^+ \rightleftharpoons Bi_2O_4 + H_2O$ $\quad E^{eq} = E^0_{Bi_2O_5/Bi_2O_4} - \frac{RT}{2F} ln \frac{[Bi_2O_5][H^+]^2}{[Bi_2O_4][H_2O]}$ → $\propto -0.059\ pH$

(6) $Bi^0 + 3H^+ + 3e^- \rightleftharpoons BiH_3$ $\quad E^{eq} = E^0_{Bi/BiH_3} - \frac{RT}{3F} ln \frac{[Bi][H^+]^3}{[BiH_3]}$ → $\propto -0.059\ pH$

Exercise1: Pourbaix diagram

5) From the Pourbaix diagram, propose boundary conditions on E, pH and $[Bi^{3+}]$ for the electrodeposition of Bi^0

The direct reduction of Bi^{3+} is prefered → no local pH change



Exercise1: Pourbaix diagram

5) From the Pourbaix diagram, propose boundary conditions on E, pH and $[Bi^{3+}]$ for the electrodeposition of Bi^0

The direct reduction of Bi^{3+} is preferred

→ no local pH change during ECD

→ pH < 2

Bi^{3+} concentration should be high

→ Increase E^{eq} by $\frac{0.059}{3} log[Bi^{3+}]$

→ Increase deposition rate

→ Limited by the salt solubity

Applied potential above $E^{eq}_{H^+/H_2}$

→ To avoid H_2 evolution (bubble formation, ECD efficiency, local pH increase)