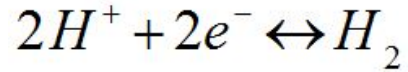

Pourbaix Diagram for Aluminum

— Nithya, Xuan, Yipin —

Possible Reactions in Al-H₂O system

Equilibria involving aluminum metal
$3 e^- + Al^{3+} = Al$
$3 e^- + Al(OH)_3 + 3 H^+ = Al + 3 H_2O$
$6e + Al_2O_3 \cdot H_2O + 6 H^+ = 2 Al + 4 H_2O$
$3 e^- + AlO_2^- + 4 H^+ = Al + 2 H_2O$
$3 e^- + Al(OH)^{2+} + H^+ = Al + H_2O$
$3 e^- + Al(OH)_2^+ + 2 H^+ = Al + 2 H_2O$
Equilibria involving solid forms of oxidized aluminum
$Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O$
$Al_2O_3 \cdot H_2O + 2 H^+ = 2 Al(OH)_2^+$
$Al(OH)_3 + 2 H^+ = Al(OH)^{2+} + 2 H_2O$
$Al_2O_3 \cdot H_2O + 4 H^+ = 2 Al(OH)^{2+} + 2 H_2O$
$Al(OH)_3 + 3 H^+ = Al^{3+} + 3 H_2O$
$Al_2O_3 \cdot H_2O + 6 H^+ = 2 Al^{3+} + 4 H_2O$
$Al(OH)_3 = AlO_2^- + H^+ + H_2O$
$Al_2O_3 \cdot H_2O = 2 AlO_2^- + 2 H^+$
Equilibria involving only soluble forms of oxidized aluminum
$AlO_2^- + 4 H^+ = Al^{3+} + 2 H_2O$

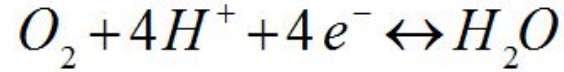
Hydrogen/Oxygen Reactions



$$E = E^\circ - (0.059/n) \log \left(\frac{[H_2]}{[H^+]^2} \right)$$

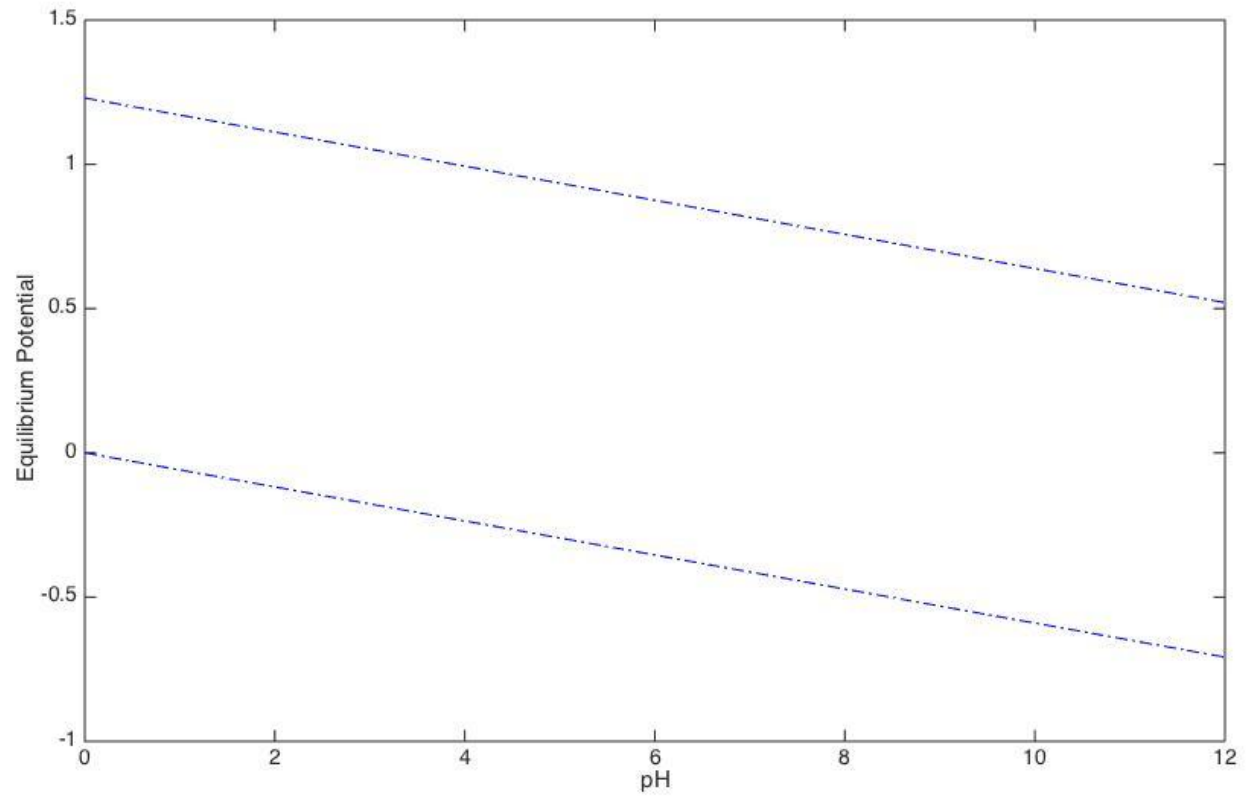
$$E_{H^+/H_2} = -0.059 \text{ pH} - 0.0295 \log p_{H_2}$$

$$E_{H^+/H_2} = -0.059 \text{ pH}$$



$$E_{O_2} = E_{O_2}^\circ - 0.01481 \log \frac{a_{H_2O}}{p_{O_2} a_{H^+}^4}$$

$$E_{O_2} = 1.230 - 0.0591 \text{ pH}$$



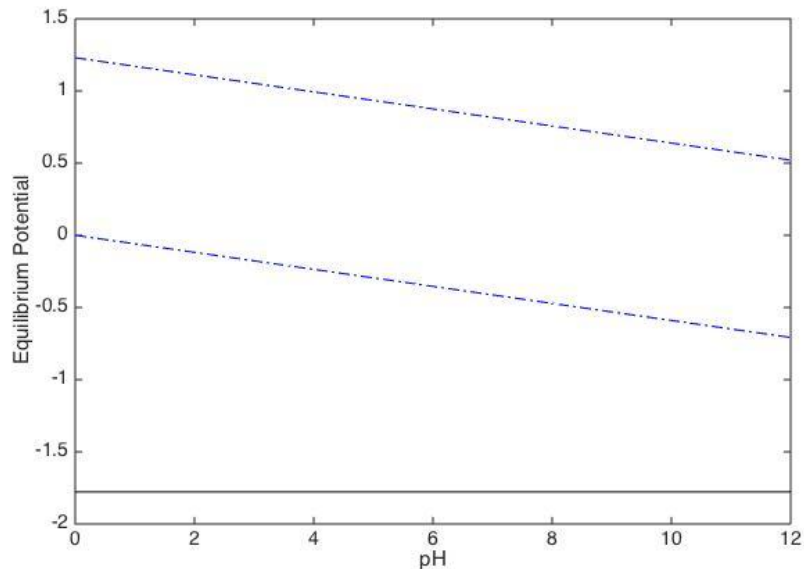
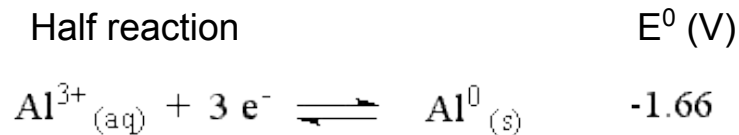
Reaction Calculations

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

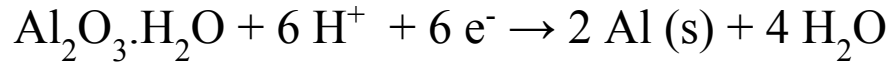


$$E = -1.66 - \frac{0.059}{3} \log \frac{1}{[\text{Al}^{3+}]}$$

$$E = -1.66 + \frac{0.059}{3} \log [\text{Al}^{3+}]$$



Reaction Calculations



$$E_{\text{Al}_2\text{O}_3/\text{Al}} = E_{\text{Al}_2\text{O}_3/\text{Al}}^{\circ} - \frac{2.303RT}{nF} \log \left(\frac{(a_{\text{Al}})^2 (a_{\text{H}_2\text{O}})^4}{a_{\text{Al}_2\text{O}_3} (a_{\text{H}^+})^2} \right)$$

$$\Delta G^{\circ} = nFE^{\circ}$$

Reaction Calculations

$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ -1825.5 kJ/mol

H_2O -237.0 kJ/mol

Al -0.0 kJ/mol

H^+ -0.0 kJ/mol

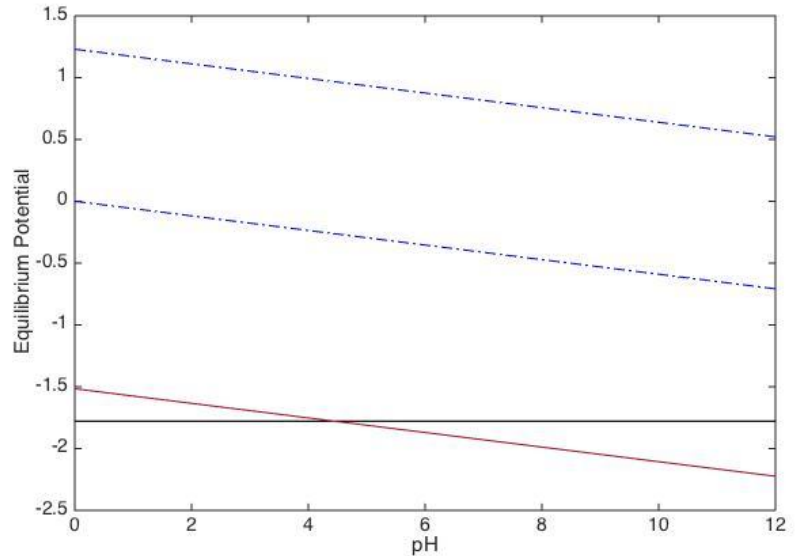
$$E^\circ = \frac{-\Delta G_{rxn}^\circ}{nF} = \frac{-[4 \times (-237.0) - (-1825.5)] \times (1000 \text{ J / kJ})}{6 \times 96485}$$

$$E^\circ = -1.516 \text{ V}$$

Reaction Calculations

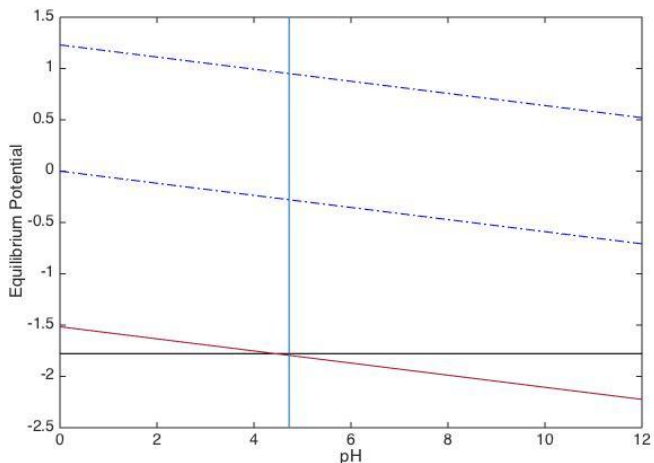
$$E_{Al_2O_3/Al} = -1.516 + 0.059 \log(a_{H^+})$$

$$E_{Al_2O_3/Al} = -1.516 - 0.059 \text{ pH}$$

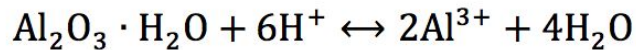


Reaction Calculations

Al^{3+}	-485.4	kJ/mol
H_2O	-237.0	kJ/mol
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	-1825.5	kJ/mol
H^+	0.0	kJ/mol



$$-\Delta G_{rxn}^{\circ} = RT \ln(K_{eq})$$



$$K_{eq} = e^{\frac{-\Delta G^{\circ}}{RT}} = \frac{a_{\text{Al}^{3+}}^2}{a_{\text{H}^+}^6}$$

$$K_{eq} = e^{\frac{-[2(-485.4) + 4(-237) - (-1825.5)] \frac{\text{kJ}}{\text{mol}} \cdot \frac{1000\text{J}}{1\text{kJ}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 298\text{K}}} = 2.2625 \times 10^{16}$$

$$\log K = 2 \log[\text{Al}^{3+}] - 6 \log[\text{H}^+]$$

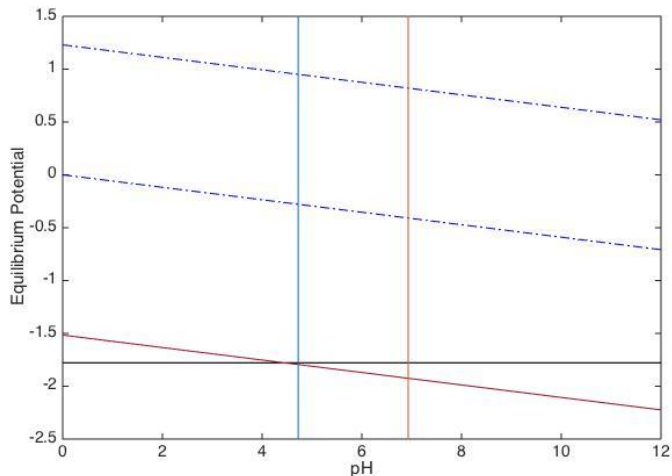
$$\text{pH} = \frac{1}{6} (\log(2.2625 \times 10^{16}) - 2 \log[\text{Al}^{3+}])$$

$$\text{pH} = \frac{1}{6} (16.35 - 2 \log[\text{Al}^{3+}])$$

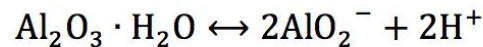
$$\text{pH} = 2.725 - 0.333 \log[\text{Al}^{3+}]$$

Reaction Calculations

AlO_2^-	-838.968	kJ/mol
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	-1825.5	kJ/mol
H^+	0.0	kJ/mol



$$-\Delta G_{rxn}^{\circ} = RT \ln(K_{eq})$$



$$K_{eq} = e^{\frac{-\Delta G^{\circ}}{RT}} = a_{\text{AlO}_2^-}^{-2} \cdot a_{\text{H}^+}^2$$

$$K_{eq} = e^{\frac{-[2(-838.968) - (-1825.5)] \frac{\text{kJ}}{\text{mol}} \cdot \frac{1000\text{J}}{1\text{kJ}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 298\text{K}}} = 1.3597 \times 10^{-26}$$

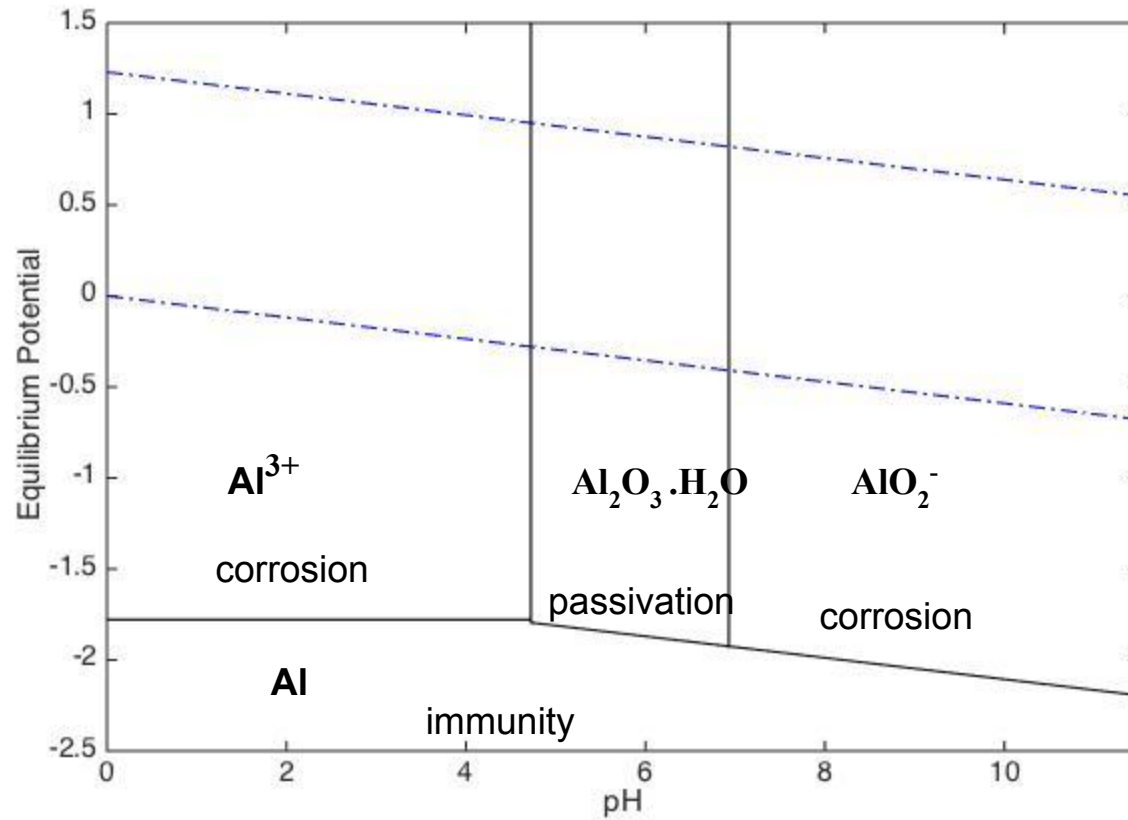
$$\log K = 2 \log[\text{H}^+] + 2 \log[\text{AlO}_2^-]$$

$$-\text{pH} = \frac{1}{2} (\log(1.3597 \times 10^{-26}) - 2 \log[\text{AlO}_2^-])$$

$$\text{pH} = \frac{1}{2} (-\log(1.3597 \times 10^{-26}) + 2 \log[\text{AlO}_2^-])$$

$$\text{pH} = \frac{1}{2} (25.867 + 2 \log[\text{AlO}_2^-])$$

$$\text{pH} = 12.93 + \log[\text{AlO}_2^-]$$



$$E_{Al^{3+}/Al} = -1.662 + 0.0197 \log(a_{Al^{3+}})$$

Al ³⁺ concentration	10 ⁻⁴	10 ⁻²	10 ⁰
E	-1.7408	-1.7014	-1.662

$$pH = 2.732 - 0.333 \log(a_{Al^{3+}})$$

Al ³⁺ concentration	10 ⁻⁴	10 ⁻²	10 ⁰
pH	4.064	3.398	2.732

$$pH = 12.93 + \log(a_{AlO_2^-})$$

AlO ₂ ⁻ concentration	10 ⁻⁴	10 ⁻²	10 ⁰
pH	8.93	10.93	12.93

