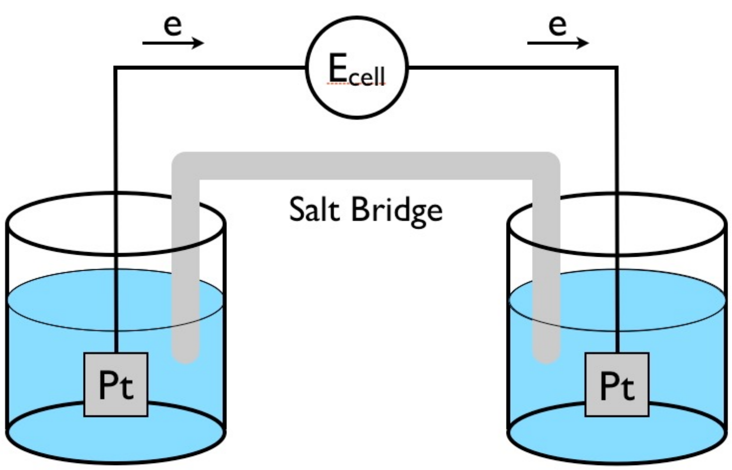
Electrochemistry: The Nernst Equation

$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$

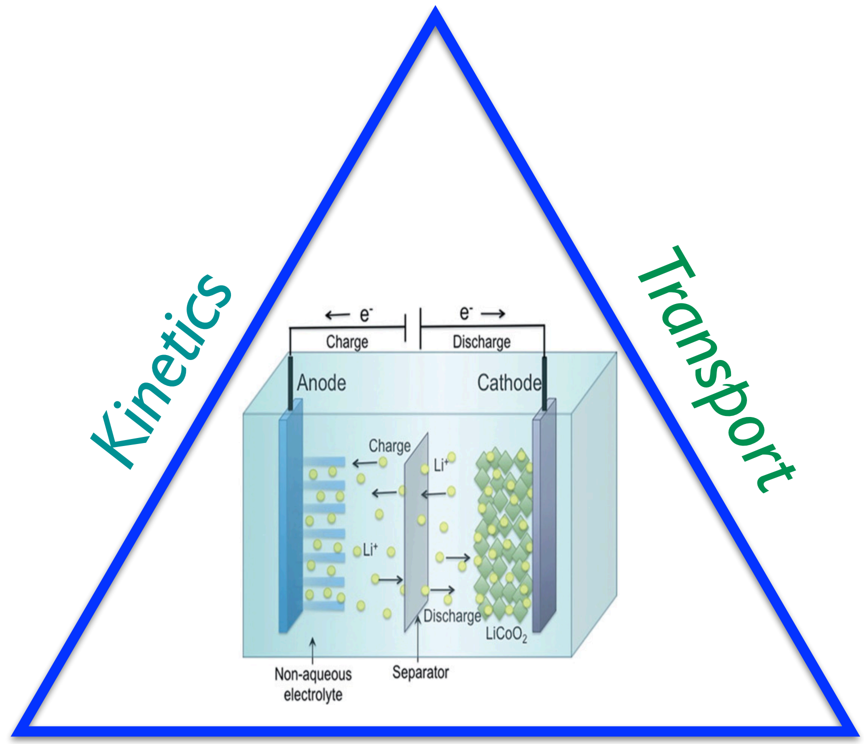


$Ce^{3+} \rightarrow Ce^{4+} + e$ | $Fe^{3+} + e \rightarrow Fe^{2+}$

Oxidation | *Reduction*

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} lnQ$$

$$\text{where } \Delta G^0 = -nFE^0_{cell}$$



Thermodynamics

↓

Nernst Equation

Prof. Rob Corn   Chem M3LC

Solution Oxidation-Reduction (Redox) Reactions

$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$

$$Ce^{3+} \rightarrow Ce^{4+} + e$$

Oxidation

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

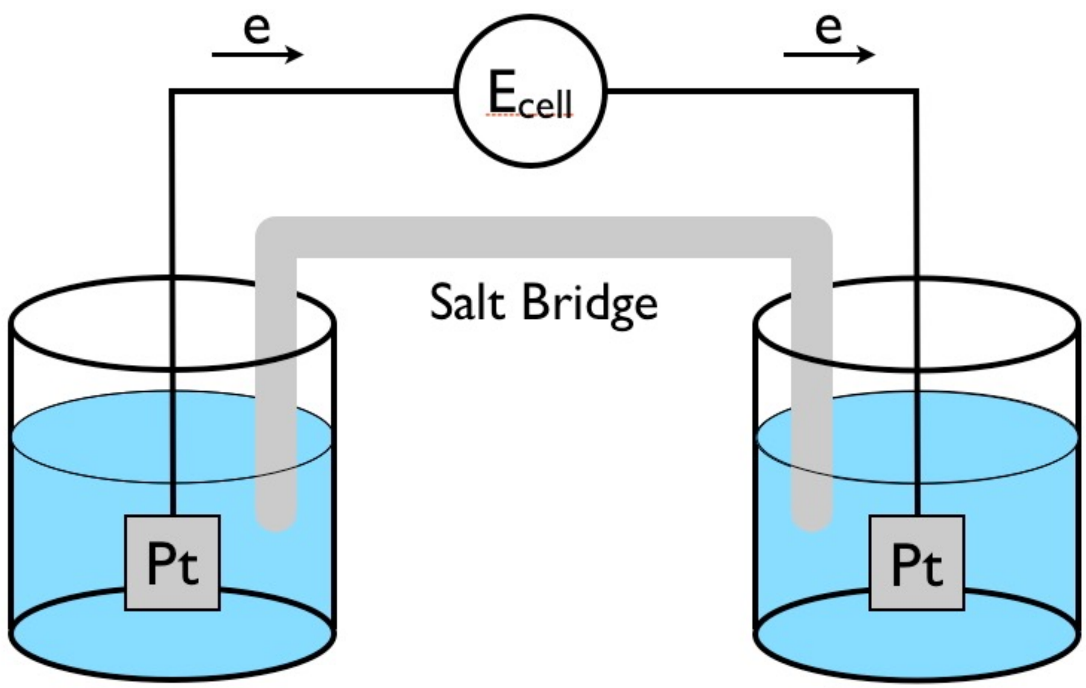
Reduction

$$Ce^{3+} \xrightarrow{e^{-}} Fe^{3+}$$

Electron Transfer Reaction

Electrochemical Oxidation-Reduction Reactions

$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$



Reduction
on the Right

$$Ce^{3+} \rightarrow Ce^{4+} + e$$

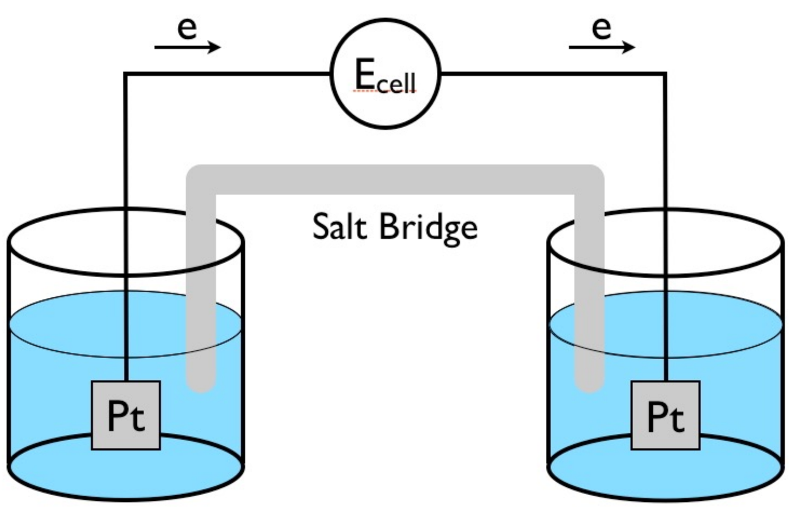
Oxidation

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

Reduction

Two separate electron transfer reactions

Nernst Equation Derivation



$Ce^{3+} \rightarrow Ce^{4+} + e$

Oxidation

$Fe^{3+} + e \rightarrow Fe^{2+}$

Reduction

$$\Delta G = -nFE_{cell}$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$-nFE_{cell} = -nFE^0_{cell} + RT \ln Q$$

Where:

n = # electrons transferred

Q = reaction quotient

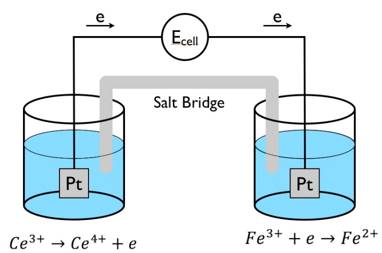
and: $\Delta G^0 = -nFE^0_{cell}$

$$\boxed{E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q}$$

Nernst Equation

Galvanic vs Electrolytic Cells

A reaction is spontaneous if



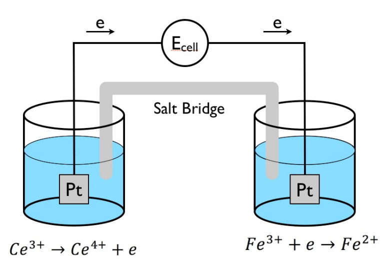
Current flows spontaneously

$$\Delta G < 0 \longrightarrow \boxed{E_{cell} > 0}$$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} > 0$$

"Galvanic Cell"

A reaction is NOT spontaneous if



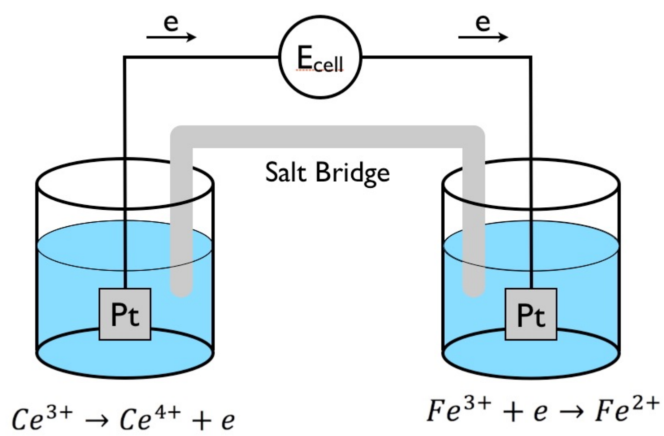
Must supply and external voltage

$$\Delta G > 0 \longrightarrow \boxed{E_{cell} < 0}$$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} < 0$$

"Electrolytic Cell"

Nernst Equation



$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$$

At Equilibrium: $\Delta G = 0$

Net reaction: $n = 1$

$$E_{cell} = -\frac{\Delta G}{nF} = 0$$

$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$

$$Q = \frac{[Fe^{2+}][Ce^{4+}]}{[Fe^{3+}][Ce^{3+}]}$$

$$\boxed{E^0_{cell} = \frac{RT}{nF} \ln K_{eq}}$$

$Q = K_{eq}$ at Equilibrium

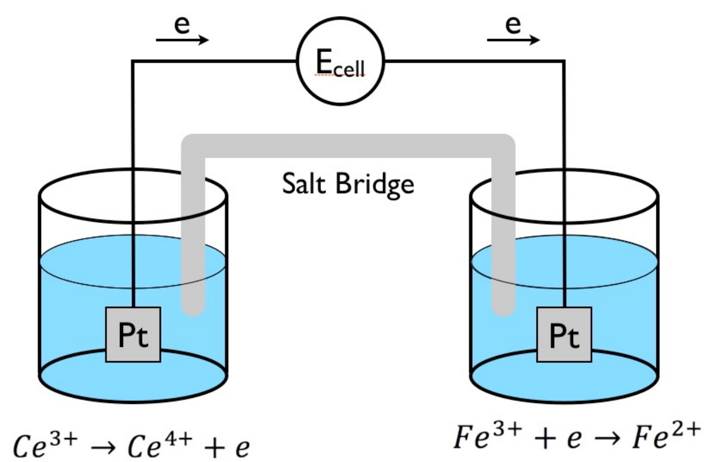
$$K_{eq} = e^{\left(\frac{nF}{RT}E^0_{cell}\right)}$$

$$nFE^0_{cell} = -\Delta G^0$$

To Calculating Cell Potentials We Break the Nernst Equation into Two Parts:

Oxidation

$$E_{ox} = E_{Ce}$$



Reduction

$$E_{red} = E_{Fe}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q = E_{red} - E_{ox} = E_{Fe} - E_{Ce}$$

E_{Ce} and E_{Fe} are called "Half Cells"

Half Cell Reactions and Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$

To Calculate the Half Cell Potential E_{Fe}

$$Fe^{3+} + e \leftrightharpoons Fe^{2+}$$

Half Cell Reaction

$n = 1$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{nF} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Half Cell Potential

E^0_{Fe} is called the standard reduction potential

look this up in a table: $\boxed{E^0_{Fe} = +0.770V}$

Half Cell Reactions and Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$

To Calculate the Half Cell Potential E_{Ce}

All Half Cell Reactions are Reductions!

$$Ce^{4+} + e \leftrightharpoons Ce^{3+}$$

Half Cell Reaction

$n = 1$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{nF} \ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Half Cell Potential

E^0_{Ce} is called the standard reduction potential

look this up in a table: $\boxed{E^0_{Ce} = +1.610V}$

Standard Half Cell Reaction for Hydrogen (NHE):

$$E_{cell} = E_{red} - E_{ox}$$

Since we always use half cell differences, we can add an arbitrary constant to all half cells. By convention, we assume that the E^{o} for the normal hydrogen electrode (NHE) is equal to zero:

$$H^{+} + e \rightarrow \frac{1}{2} H_{2(g)}$$

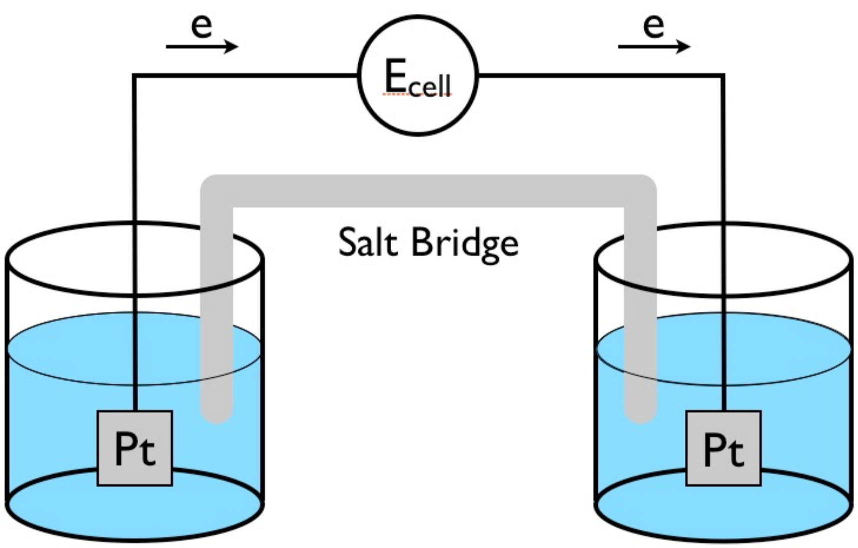
$$E_H = E_H^0 - \frac{RT}{F} ln \frac{{P_{H_2}}^{1/2}}{[H^+]} \qquad E_H^0 = 0$$

Thus we say: $E_{Fe}^{0} = +0.770V$ *"vs. NHE"*

$E_{Ce}^{0} = +1.610V$ *"vs. NHE"*

Half Cell Potentials

Half Cell Potentials are ALWAYS tabulated as reductions:



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

Oxidation

$$E_{Ce}$$

$$E^0_{Ce} = +1.610V$$

Reduction

$$E_{Fe}$$

$$E^0_{Fe} = +0.770V$$

$$E_{cell} = E_{Fe} - E_{Ce}$$

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

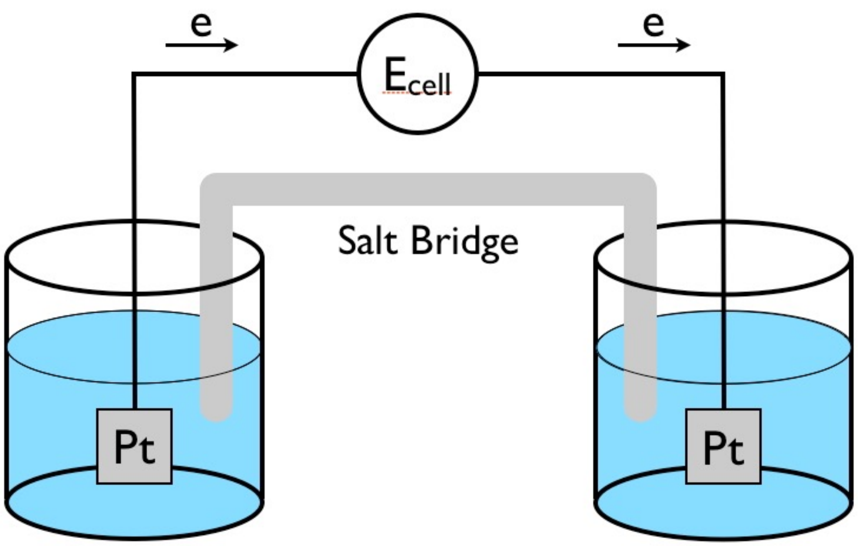
$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

We only measure E_{cell} - we never measure half cell potentials

We can calculate E^0_{cell} from the standard reduction potentials:



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

Oxidation

Reduction

$$E_{Ce}$$

$$E_{Fe}$$

$$E^0_{Ce} = +1.610V$$

$$E^0_{Fe} = +0.770V$$

$$E^0_{cell} = E^0_{Fe} - E^0_{Ce}$$

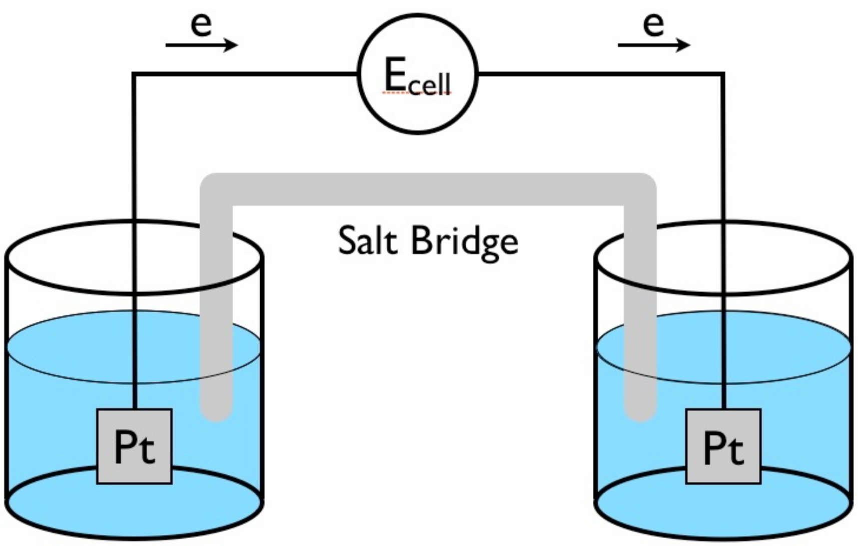
$$= +0.770V - 1.610V$$

$$E^0_{cell} = -0.910V$$

If Q=1, $E_{cell} = E^0_{cell}$

Is this reaction spontaneous?

We can calculate E^0_{cell} from the standard reduction potentials:



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

$$E^0_{cell} = E^0_{Fe} - E^0_{Ce}$$

$$= +0.770V - 1.610V$$

$$E^0_{cell} = -0.910V$$

Oxidation

$$E_{Ce}$$

$$E^0_{Ce} = +1.610V$$

Reduction

$$E_{Fe}$$

$$E^0_{Fe} = +0.770V$$

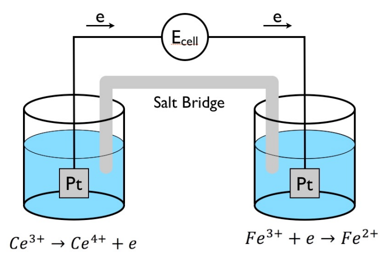
Not Spontaneous!
Electrolytic Cell!

$$E^0_{cell} = -\frac{\Delta G^0}{nF}$$

The reverse reaction is spontaneous: Galvanic Cell.

Galvanic vs Electrolytic Cells

A reaction is spontaneous if



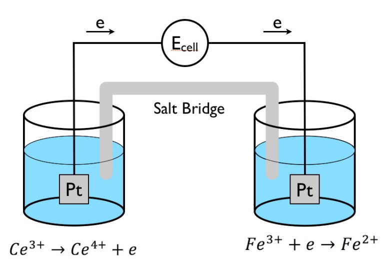
Current flows spontaneously

$$\Delta G < 0 \longrightarrow \boxed{E_{cell} > 0}$$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} > 0$$

"Galvanic Cell"

A reaction is NOT spontaneous if



Must supply and external voltage

$$\Delta G > 0 \longrightarrow \boxed{E_{cell} < 0}$$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} < 0$$

"Electrolytic Cell"

Example #1: Electrolysis of Water

$$2H_2O \leftrightharpoons 2H_{2(g)} + O_{2(g)}$$

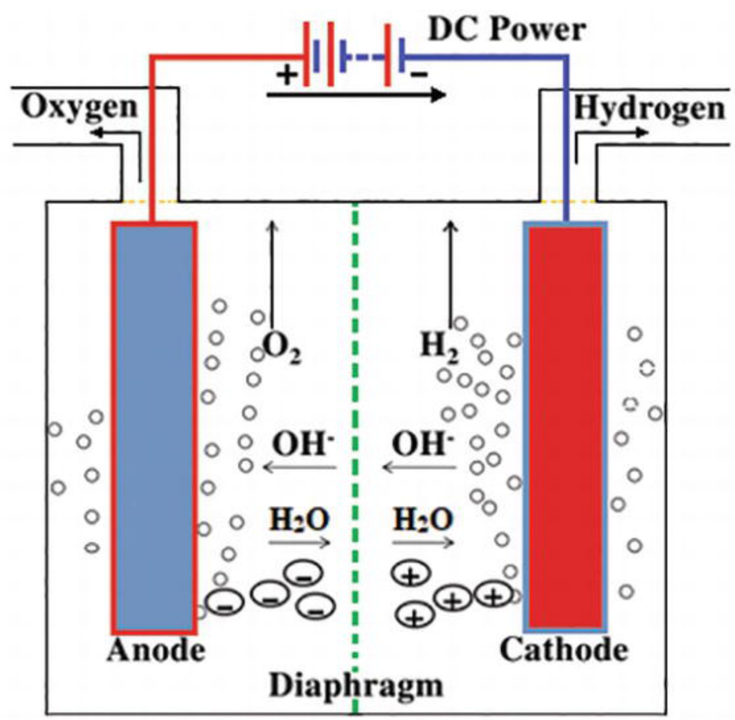
At the positively charged anode, an oxidation reaction occurs, generating oxygen gas (these equations are for acidic pH):

Spontaneous?

Oxidation at anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e$

At the negatively charged cathode, a reduction reaction occurs, generating hydrogen gas:

Reduction at cathode: $2\ H^+(aq) + 2e^- \rightarrow H_2(g)$



Half Cell Potentials:

$O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2\ H_2O(l)$ $E° = +1.229\ V$

$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$ $E° = -0.8277\ V$

$E°(cell) = E°(red) - E°(ox) = -0.8277 – 1.229 = -2.056\ V$

Example #1: Electrolysis of Water

$$2H_2O \leftrightharpoons 2H_{2(g)} + O_{2(g)}$$

At the positively charged anode, an oxidation reaction occurs, generating oxygen gas (these equations are for acidic pH):

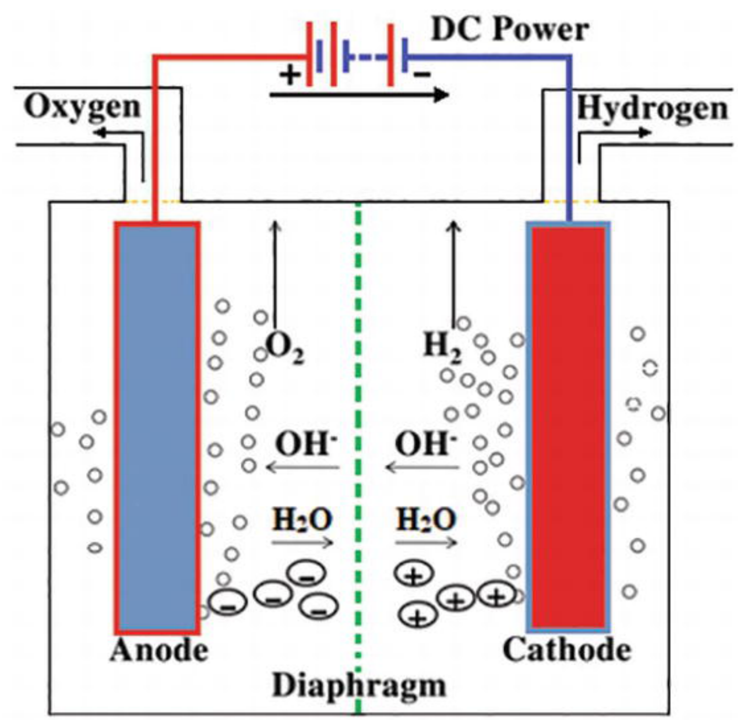
Oxidation at anode: 2 H_2O(*l*) → O_2(*g*) + 4 H^+(*aq*) + 4e

$$\mathbf{E}_{cell} < 0$$

Not Spontaneous: Electrolytic Cell!

At the negatively charged cathode, a reduction reaction occurs, generating hydrogen gas:

Reduction at cathode: 2 H^+(*aq*) + 2e^- → H_2(*g*)



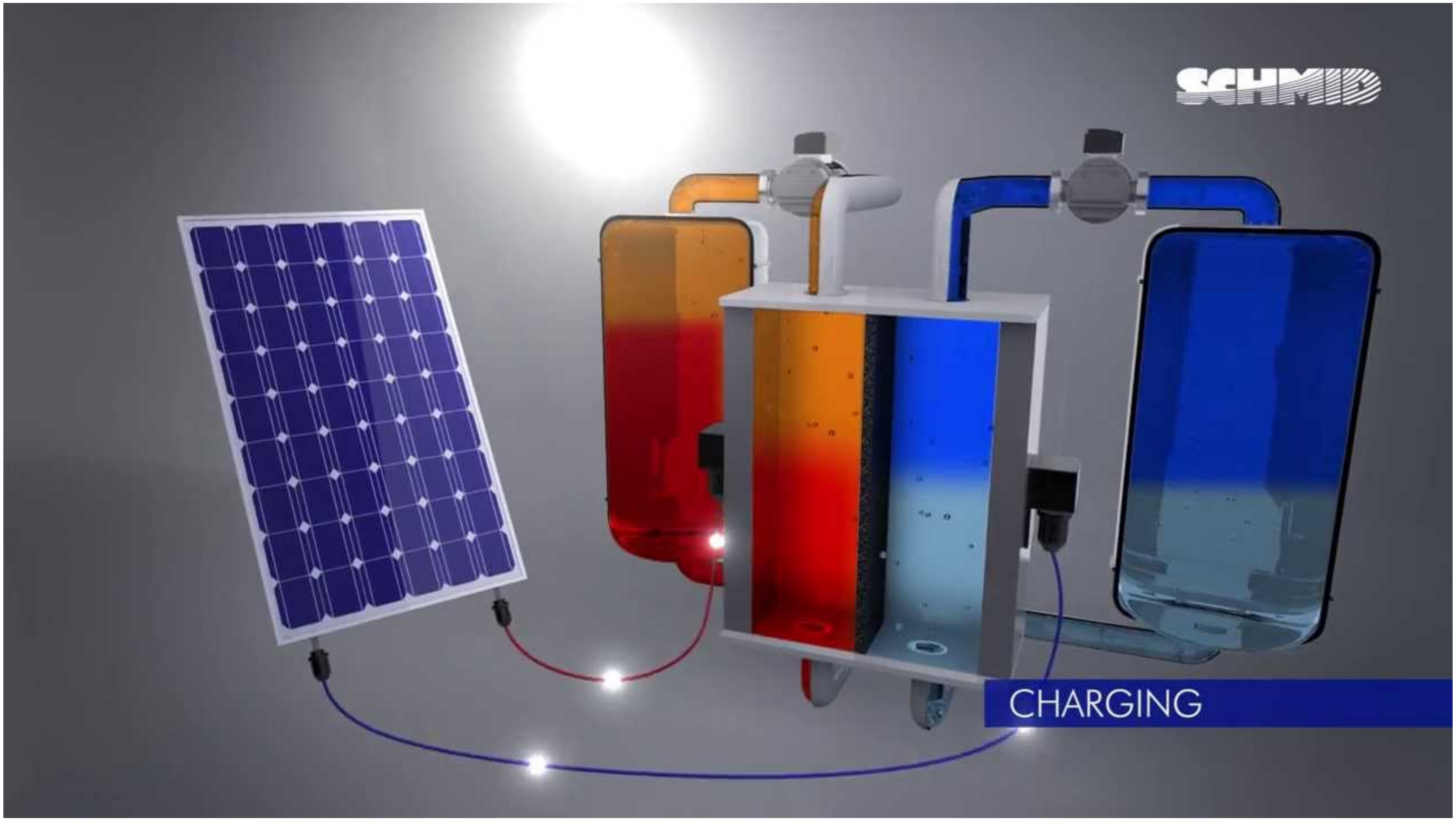
Half Cell Potentials:

O_2(*g*) + 4 H^+(*aq*) + 4e^- → 2 H_2O(*l*)   E° = +1.229 V

2 H^+(*aq*) + 2e^- → H_2(*g*)   E° = -0.8277 V

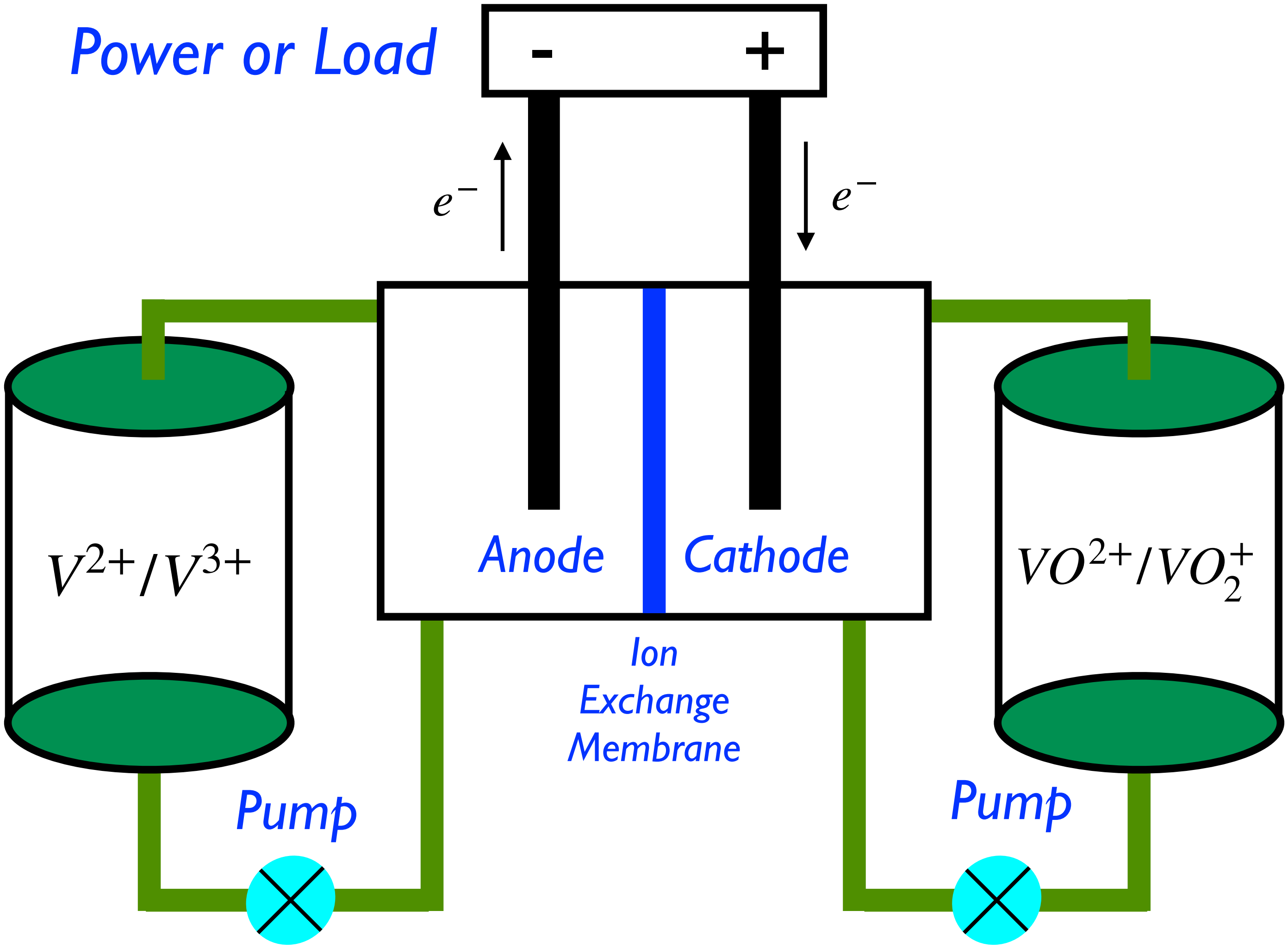
E°(cell) = E°(red) - E°(ox) = -0.8277 – 1.229 = -2.056 V

Example #2: Vanadium Redox Flow Battery



Solar Panel Charging

Example #2: Vanadium Redox Flow Battery



Four stable oxidation states:

$V^{2+}, V^{3+},$
VO^{2+}, VO_2^{+}

$$E_{cell} = E_{Red} - E_{Ox}$$

$$V^{2+} \rightleftharpoons V^{3+} + e^{-}$$

Oxidation

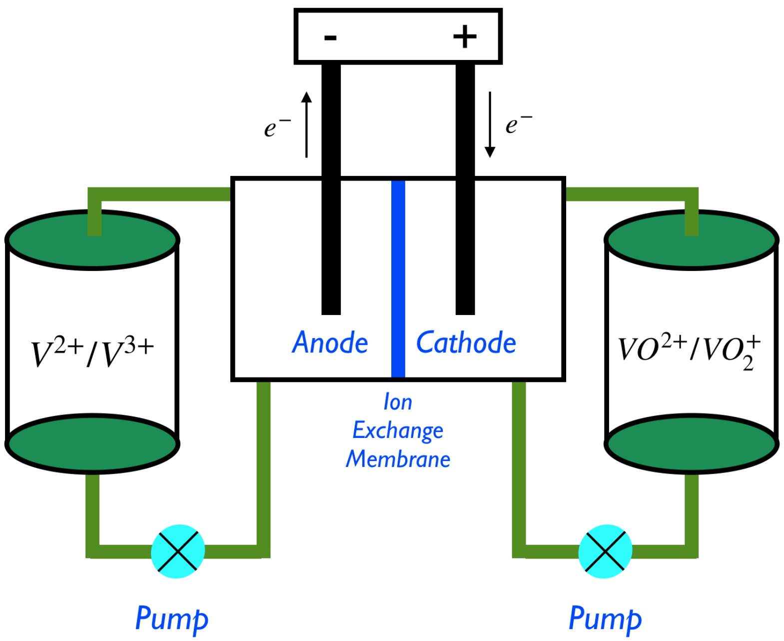
E_{Ox}

$$VO_2^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_2O$$

Reduction

E_{Red}

Example #2: Vanadium Redox Flow Battery



$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

Cathode Half Cell Potential: E^0_{red} = 1.00V

$$V^{3+} + e^- \rightleftharpoons V^{2+}$$

Anode Half Cell Potential: E^0_{ox} = -.26V

$$E^0_{cell} = E^0_{red} - E^0_{ox}$$

$$E^0_{cell} = 1.00V - (-0.26V) - = +1.26V$$

Spontaneous Discharge Reaction

Vanadium Redox Flow Battery

Canadian Installation

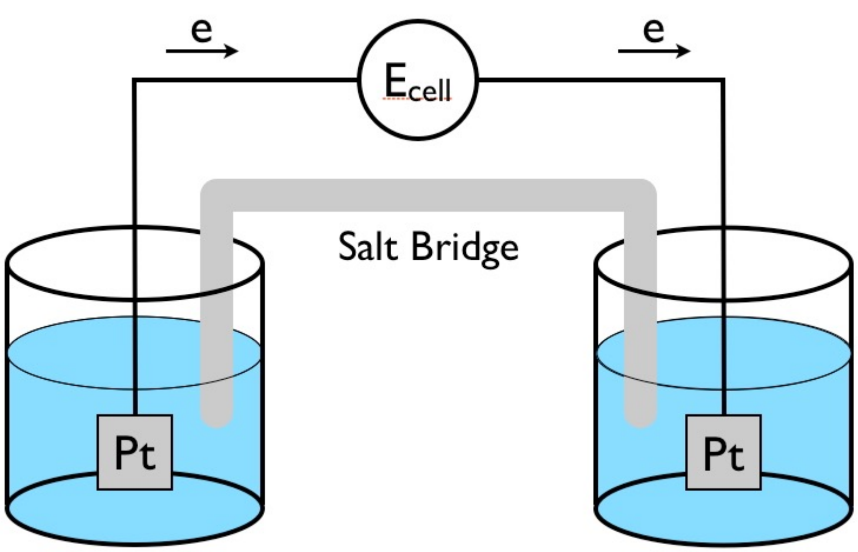
Vanadium Redox Flow Battery

Vanadium Oxidation States

$$V^{2+} \qquad V^{3+} \qquad VO^{2+} \qquad VO_2^+$$

World's Largest Battery? 200MW/800MWhr

Nernst Equation



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

Oxidation

Reduction

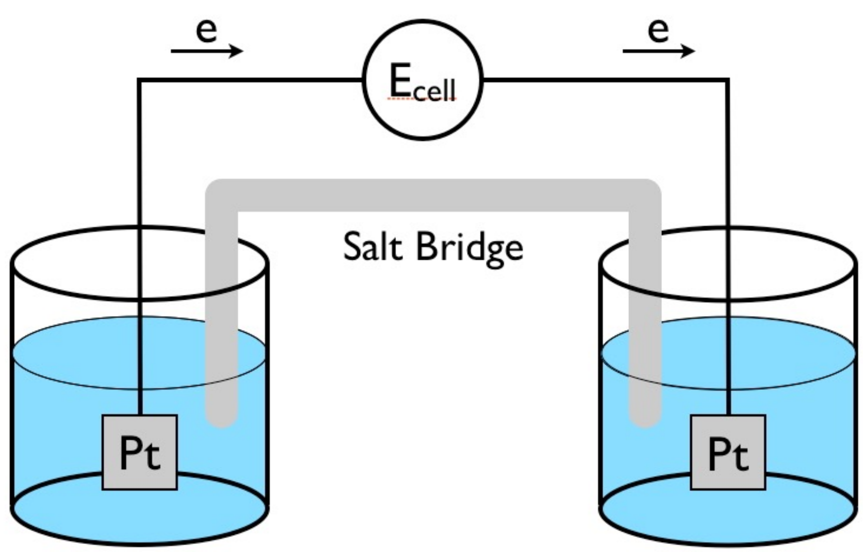
$$\Delta G = -nFE_{cell}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q$$

Net reaction: $Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$

$$Q = \frac{[Fe^{2+}][Ce^{4+}]}{[Fe^{3+}][Ce^{3+}]}$$

Nernst Equation - Half Cell Potentials



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

$$E_{cell} = E_{red} - E_{ox}$$

To calculate the cell potential, we use two half cells corresponding to the reduction and oxidation half reactions.

Oxidation

$$E_{Ce}$$

Reduction

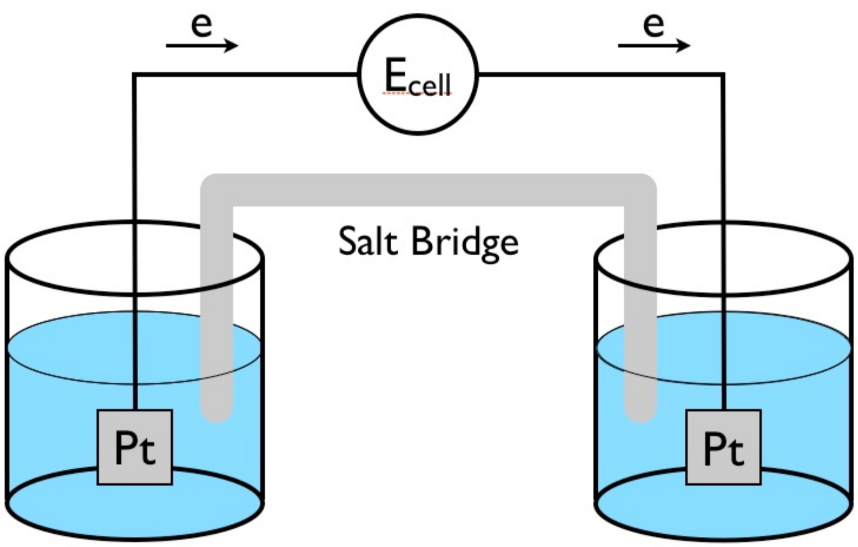
$$E_{Fe}$$

$$E_{cell} = E_{Fe} - E_{Ce}$$

Half Cell Potentials are ALWAYS tabulated and calculated as reductions

Nernst Equation - Half Cell Potentials

Half Cell Potentials are ALWAYS tabulated and calculated as reductions:



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

$$E_{cell} = E_{Fe} - E_{Ce}$$

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Oxidation

$$E_{Ce}$$

$$E^0_{Ce} = +1.610V$$

Reduction

$$E_{Fe}$$

$$E^0_{Fe} = +0.770V$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

We only measure E_{cell} - we never measure half cell potentials