Standard Electrode Potentials (ε^{o})

we will be concerned with standard reduction potentials

for half reactions written as reductions (electrons as reactants)

all substances in their standard state

Standard Electrode Potentials (ε^{o})

just as the over all cell reaction can be thought of as the sum of two half-cell reactions

the measured emf of the cell can be treated as the sum of the electrical potentials.

It is impossible however to measure the potential of a single electrode.

The standard hydrogen electrode*

reference all reduction half-reactions to:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \quad \varepsilon^o = 0.0\ V$$

is assigned the arbitrary potential value of 0 volts

***H_2 pressure = 1atm; [HCl] = 1M**

Standard Electrode Potentials (ε^{o})

$$\varepsilon^{o}_{cell} = \varepsilon^{o}_{ox} + \varepsilon^{o}_{red}$$

The reaction

$$2H^+(aq\,) \quad + \quad Zn(s) \quad \longrightarrow \quad H_2(g\,) \;+\; Zn^{2+}(aq)$$

represented by the cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1\,M) \parallel H^+(aq, 1\,M) \mid H_2(g, 1\text{ atm}) \mid Pt(s)$$

has a standard cell potential $\varepsilon^{o} = 0.76\text{ V}$

by convention:

$$2H^+(aq, 1\,M\,) \quad + \quad 2e^- \quad \longrightarrow \qquad 0\text{ V}$$

0.76 V is the standard oxidation potential for Zn/Zn^{2+}

therefore:

$$Zn(s) \longrightarrow Zn^{2+}(aq, 1\,M) \;+\; 2e^- \quad \varepsilon^{o} = 0.76\text{ V}$$

the custom is to tabulate ε^{o} values for half-reactions written as reductions

the standard oxidation potential for the half-reaction:

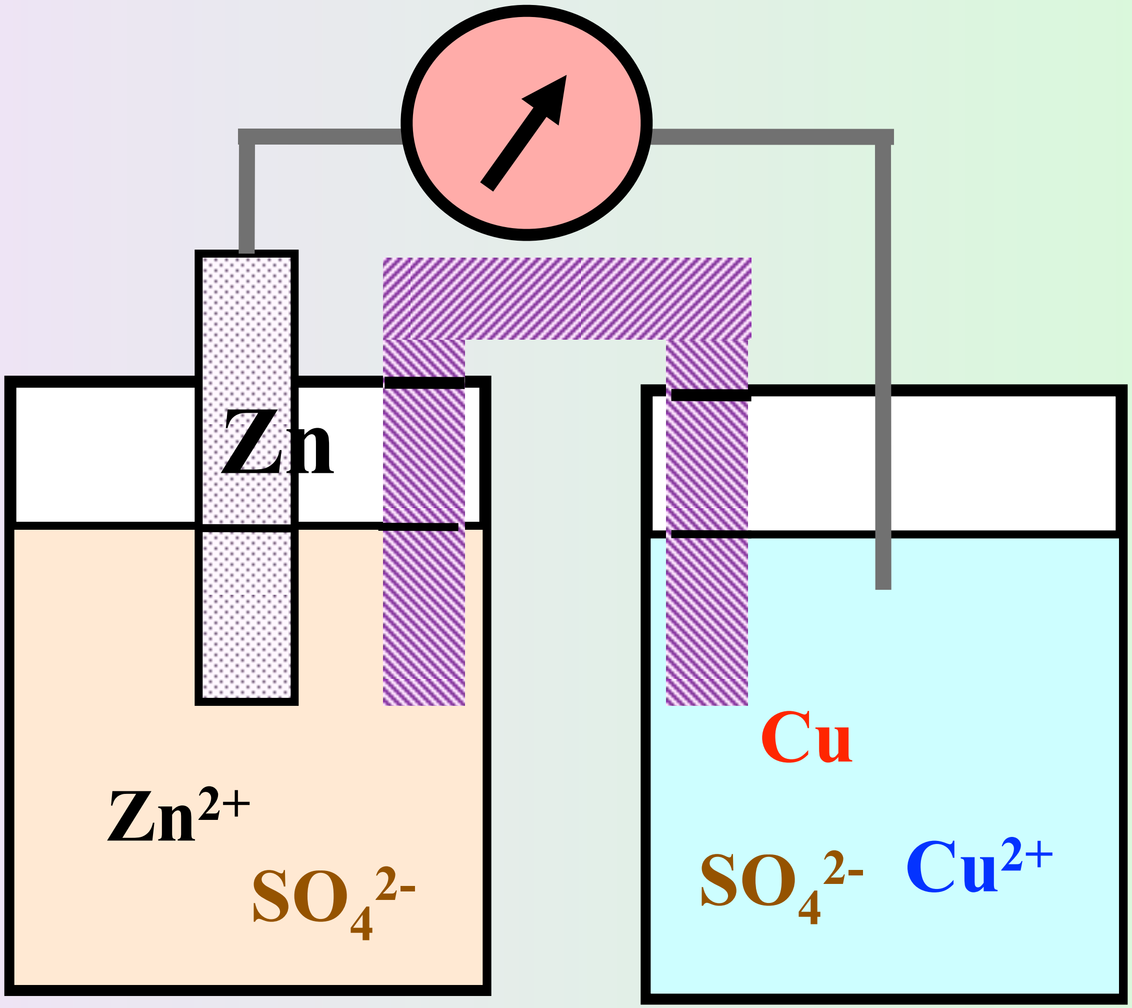
$$Zn(s) \longrightarrow Zn^{2+}(aq, 1\,M) + 2e^{-} \quad \varepsilon^{o} = 0.76\ V$$

the standard reduction potential for the half-reaction:

$$Zn^{2+}(aq, 1\,M) + 2e^{-} \longrightarrow Zn(s) \quad \varepsilon^{o} = -\,0.76\ V$$

Cell potential = 1.10 *V*

Recall the galvanic cell



when all species are in their standard state

use the measured standard cell potential and the standard reduction potential of Zn^{2+} to calculate the standard reduction potential of Cu^{2+}

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

$$\varepsilon^{o} = 1.10\ V$$

$$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s) \qquad \varepsilon^{o} = -0.76\ V$$

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-} \qquad \varepsilon^{o} = 0.76\ V$$

Therefore:

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$

$$\varepsilon^{o} = 1.10\ V - 0.76\ V = +0.34\ V$$

Standard Reduction Potentials

ε^{o} values refer to standard reduction potentials

the more positive the value of ε^{o}, the better the oxidizing agent

Standard Reduction Potentials

Better reducing agent

	ε^{o}
$Li^+(aq) + 1e^- \longrightarrow Li(s)$	-3.05 V
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76 V
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00 V
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34 V
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87 V

Better oxidizing agent

An Analogy

$$\text{acid} + \text{base} \rightleftarrows \underset{\text{acid}}{\text{conjugate}} + \underset{\text{base}}{\text{conjugate}}$$

K > 1 when

Stronger acid ⟶ Weaker acid

as measured by K_a

An Analogy

oxidizing agent + reducing agent $\rightleftarrows$ oxidized material + reduced material

K > 1 when

Stronger oxidant $\longrightarrow$ Weaker oxidant

as measured by ε^{o}

Example

Can Zn^{2+} (aq) oxidize Sn under standard state conditions?

$$Zn^{2+}(aq) + Sn(s) \longrightarrow Zn(s) + Sn^{2+}(aq)$$

What are the half- reactions?

$$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s) \qquad \varepsilon^{o} \quad -0.76\ V$$

$$Sn^{2+}(aq) + 2e^{-} \longrightarrow Sn(s) \qquad \varepsilon^{o} \quad -0.14\ V$$

Zn^{2+} is a worse oxidizing agent then Sn^{2+};

Zn^{2+} will not oxidize Sn

Example: what is the cell potential?

	ε^{o}
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76 V
$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$	+0.14 V

$$Zn^{2+}(aq) + Sn(s) \longrightarrow Zn(s) + Sn^{2+}(aq)$$

-0.62 V

If the sign is negative; the reaction is not spontaneous in the direction written.

Standard Reduction Potentials

Better reducing agent

ε^{o}

$Li^{+}(aq) + 2e^{-} \longrightarrow Li(s)$	**-3.05 V**
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	**-0.76 V**
$Sn^{2+}(aq) + 2e^{-} \longrightarrow Sn(s)$	**- 0.14 V**
$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$	**0.00 V**

Better oxidizing agent

Example: **What is the the standard emf of a galvanic cell made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution?**

$$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \qquad \varepsilon^o = -0.40\ V$$

$$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s) \qquad \varepsilon^o = -0.74\ V$$

reverse the equation with more negative ε^o and add

$$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \qquad \varepsilon^o = -0.40\ V$$

$$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^- \qquad \varepsilon^o = +0.74\ V$$

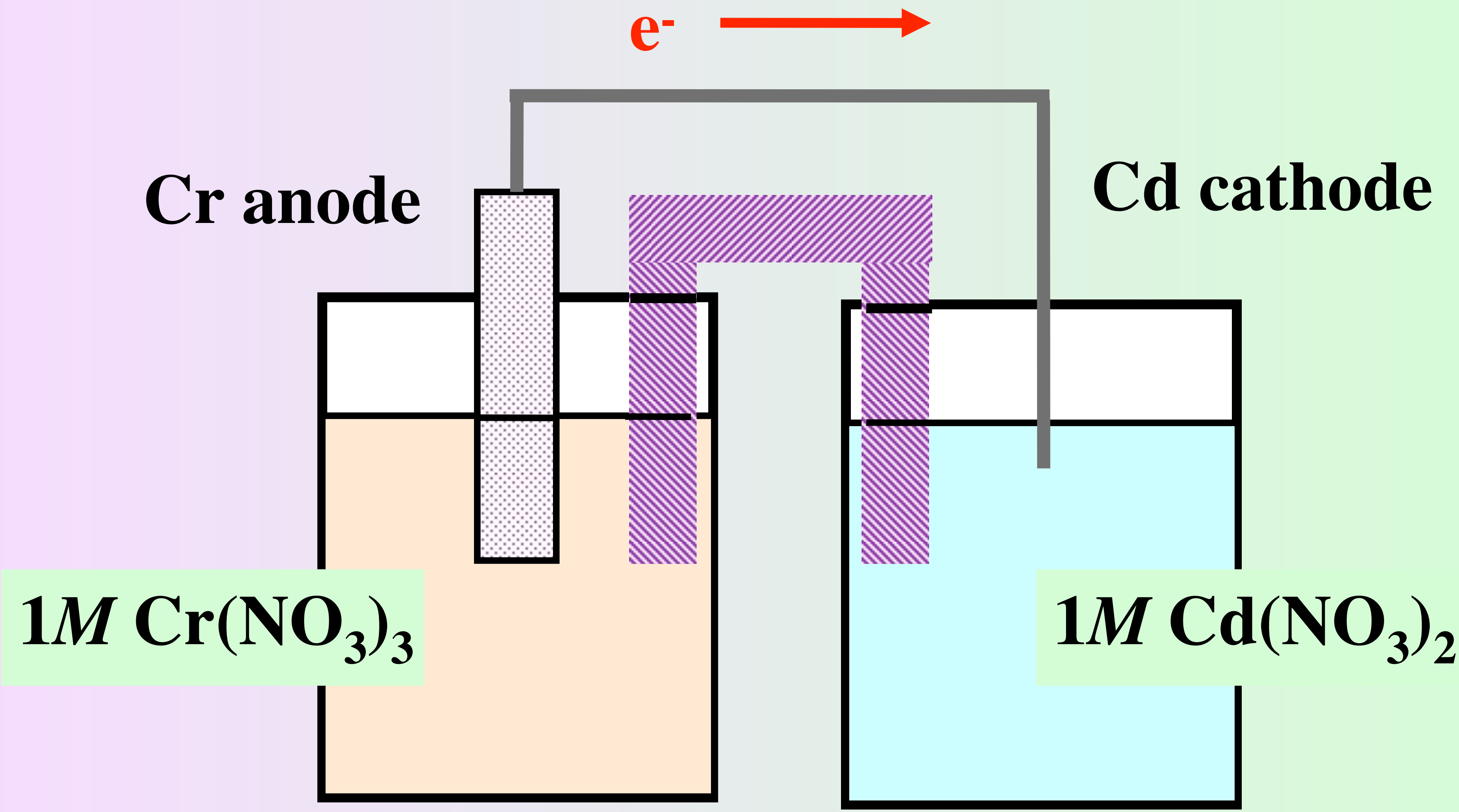
$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s) \quad \varepsilon^o = 0.34\ V$$

$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

$$\varepsilon^{o} = 0.34\ V$$

ε^{o} is an intensive property

so multiplying the reduction of Cd^{2+} by 3 and the oxidation of Cr by 2 has no effect on the value of the voltage



emf = 0.34 V