Focus 6: Chemical equilibrium

- The equilibrium constant
- The response of equilibria to the conditions
- **Electrochemical cells**
- **Electrode potentials**





electrode at which oxidation occurs



electrode at which reduction occurs

electrode at which oxidation occurs

Has a lower potential



electrode at which reduction occurs

Has a higher potential

#### Salt bridge



# Salt bridge



Salt bridge:

• Completes the Circuit

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Salt bridge:

- Completes the Circuit
- Maintains Electrical Neutrality

**LAW:** Electrochemical cells rely on different types of electrodes depending on the redox reactions involved and the design of the device. These include metal–metal ion, gas, and metal–metal salt electrodes.

Your task: Find one real-world example (not from class) for each of the following types of electrodes:

- 1. Metal–metal ion electrode
- 2. Gas electrode
- 3. Metal-metal salt electrode (e.g., Ag/AgCl)

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For each example:

- Describe where the electrode is used (e.g., a battery, fuel cell, medical sensor, industrial process, etc.).
- Write the half-cell reaction that occurs at the electrode.
- Briefly explain why that type of electrode is well-suited for the application.

 $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$ 









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

**Reduction half-reaction** 





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

cell reaction

#### $\text{Electrical Work} = q \times V$

#### Where:

- q =charge (in coulombs, C)
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Nernst equation

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at 25 °C,
$$E_{\text{cell}} = E_{\text{cell}}^{\oplus} - \frac{25.7 \,\text{mV}}{v} \ln Q$$

# Cells at equilibrium

A chemical reaction at equilibrium cannot do work!

(it generates zero potential difference between the electrodes of a galvanic cell)



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$$E_{\text{cell}} = 0 \text{ and } Q = K$$
$$I_{\text{cell}}^{\ominus} = \frac{RT}{vF} \ln K$$



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Allows us to predict equilibrium constant

## Electrochemical cells



#### GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.



#### ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation is at Anode

$$\mathbf{L} \| \mathbf{R} \quad E_{\text{cell}}^{\ominus} = E^{\ominus}(\mathbf{R}) - E^{\ominus}(\mathbf{L})$$

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Standard hydrogen electrode (SHE)

$$\mathbf{L} \| \mathbf{R} \quad E_{\text{cell}}^{\ominus} = E^{\ominus}(\mathbf{R}) - E^{\ominus}(\mathbf{L})$$

 $Pt(s)|H_2(g)|H^+(aq) = 0$  at all temperatures

The activity of the hydrogen ions must be 1 and the pressure of the hydrogen gas must be 1 bar.



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Inert Pt electrode  $2H^+(aq) + 2e^- \Rightarrow H_2(g)$  100 kPa 298 K 1 mol dm<sup>-3</sup> H<sup>+</sup>(aq)

Standard

hydrogen

electrode (SHE)

Couple	$E^{\ominus}/V$
$Ce^{4+}(aq) + e^{-} \rightarrow Ce^{3+}(aq)$	+1.61
$\operatorname{Cu}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \to \operatorname{Cu}(s)$	+0.34
$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$	+0.22
$\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \frac{1}{2}\mathrm{H}_{2}(\mathrm{g})$	0
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \to \operatorname{Zn}(s)$	-0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71

## Reducing and oxidizing agents



Example

$$\mathbf{L} \| \mathbf{R} \quad E_{\text{cell}}^{\ominus} = E^{\ominus}(\mathbf{R}) - E^{\ominus}(\mathbf{L})$$

The cell  $Ag(s)|AgCl(s)|HCl(aq)|O_2(g)|Pt(s)$  can be regarded as formed from the following two electrodes,

Electrode	Half-reaction	Standard potential
$Pt(s) O_2(g) H^+(aq)$	$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	+1.23 V
Ag(s) AgCl(s) Cl <sup>-</sup> (aq)	$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$	+0.22 V
	$E_{\text{cell}}^{\ominus} =$	

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	$E_{\text{cell}}^{\ominus} =$	$+1.01\mathrm{V}$

#### Electrochemical series

Stronger oxidizing agent

$F_2(g) + 2e^-$	$\longrightarrow 2 F(aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78
$MnO_4^{-}(aq) + 8 H^{+}(aq) + 5 e^{-}$	$\longrightarrow$ Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(l)	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2 \operatorname{Cl}^{-}(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e$	$e^- \longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l)$	1.33
$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23
$Br_2(l) + 2 e^-$	$\longrightarrow$ 2 Br <sup>-</sup> (aq)	1.09
$Ag^{+}(aq) + e^{-}$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^{-}$	$\longrightarrow$ Fe <sup>2+</sup> (aq)	0.77
$O_2(g) + 2 H^*(aq) + 2 e^-$	$\longrightarrow$ H <sub>2</sub> O <sub>2</sub> (aq)	0.70
$I_2(s) + 2 e^-$	$\longrightarrow 2 I^{-}(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^{-1}$	$\longrightarrow 4 \text{ OH}^{-}(aq)$	0.40
$Cu^{2*}(aq) + 2e^{-}$	$\longrightarrow$ Cu(s)	0.34
$Sn^{4+}(aq) + 2 e^{-}$	$\longrightarrow$ Sn <sup>2+</sup> ( <i>aq</i> )	0.15
$2 H^{*}(aq) + 2 e^{-}$	$\longrightarrow$ H <sub>2</sub> (g)	0
$Pb^{2+}(aq) + 2e^{-}$	$\longrightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Ni(s)	-0.26
$Cd^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Cd(s)	-0.40
$Fe^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Fe(s)	-0.45
$Zn^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Zn(s)	-0.76
$2 H_2O(l) + 2 e^{-1}$	$\longrightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)	-0.83
$Al^{3+}(aq) + 3e^{-}$	$\longrightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Mg(s)	-2.37
$Na^{+}(aq) + e^{-}$	$\longrightarrow$ Na(s)	-2.71
$Li^{+}(aq) + e^{-}$	$\longrightarrow$ Li(s)	-3.04

standard potentials

A a measure of the tendency of a half-reaction to occur as a reduction (gain of electrons) relative to the standard hydrogen electrode (SHE) under standard conditions (25°C, 1 atm pressure, 1 M concentration of ions).

> Stronger reducing agent

#### Electrochemical series

#### standard potentials

Stronger	$F_2(g) + 2 e^-$	$\longrightarrow 2 F(aq)$	2.87
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agent	$Li^{+}(aq) + e^{-}$	$\longrightarrow$ Li(s)	-3.04

Weaker reducing agent

Stronger

reducing

agent

cell reaction  $2 \operatorname{Cu}^+(\operatorname{aq}) \rightarrow \operatorname{Cu}(s) + \operatorname{Cu}^{2+}(\operatorname{aq})$ 

A disproportionation reaction

cell reaction  $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$  A disproportionation reaction

R: Cu(s)|Cu<sup>+</sup>(aq) L: Pt(s)|Cu<sup>2+</sup>(aq),Cu<sup>+</sup>(aq) Cu<sup>+</sup>(aq) + e<sup>-</sup> → Cu(s) E<sup>⊖</sup>(R) = +0.52 VCu<sup>2+</sup>(aq) + e<sup>-</sup> → Cu<sup>+</sup>(aq) E<sup>⊖</sup>(L) = +0.16 V

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 $RT/F = 0.025\,693\,V$ 

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$$E_{\rm cell}^{\oplus} = 0.52 \,\mathrm{V} - 0.16 \,\mathrm{V} = +0.36 \,\mathrm{V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\oplus} - \frac{RT}{vF} \ln Q$$
$$E_{\text{cell}}^{\oplus} = \frac{RT}{vF} \ln K \qquad v = 1$$
$$RT/F = 0.02569$$

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 $E_{\rm cell}^{\odot} = 0.52 \,\mathrm{V} - 0.16 \,\mathrm{V} = +0.36 \,\mathrm{V}$ 

 $E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{\nu F} \ln Q$ 

 $E_{\text{cell}}^{\oplus} = \frac{RT}{vF} \ln K$ 

$$\ln K = \frac{0.36 \,\mathrm{V}}{0.025\,693 \,\mathrm{V}} = 14.0...$$
$$K = 1.2 \times 10^{6}.$$

 $RT/F = 0.025\,693\,V$ 

v = 1

#### CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics