

## Determination of Electrode Potentials

- Electrode potentials can be determined by measurements versus the standard H-electrode or other electrodes with known potentials

**Example:**  $E^\circ_{cell} = +0.46 \text{ V}$  for the reaction:



If  $E^\circ = +0.34 \text{ V}$  for the  $\text{Cu}^{2+}/\text{Cu}$  redox couple, what is  $E^\circ$  for the  $\text{Ag}^+/\text{Ag}$  redox couple?

→ Split into half-reactions:



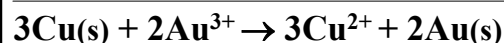
$$E^\circ_{cell} = E^\circ_{\text{Ag}} - E^\circ_{\text{Cu}} = E^\circ_{\text{Ag}} - (+0.34) = +0.46$$

$$\Rightarrow E^\circ_{\text{Ag}} = +0.46 + (+0.34) = +0.80 \text{ V}$$

## Using Cell Potentials in Calculations

- Cell potentials are **additive**
  - If two reactions are added, their potentials are added too
- Cell potentials are **intensive properties** – remain independent of the system size
  - If a reaction (or a half-reaction) is multiplied by a number, its potential remains the same

**Example:**



$$E^\circ_{cell} = +0.46 + 0.70 = +1.16 \text{ V}$$

## Strengths of Oxidizing and Reducing Agents

- $E^\circ$  values are always tabulated for **reduction**



- **Ox** is an oxidizing agent; **Red** is a reducing agent
- $E^\circ$  is a measure for the tendency of the half-reaction to undergo reduction

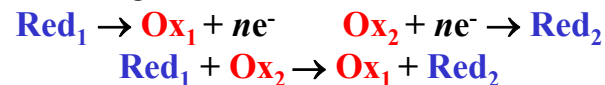
⇒ **Higher** (more positive)  $E^\circ$  means

- Greater tendency for reduction
- Lower tendency for oxidation

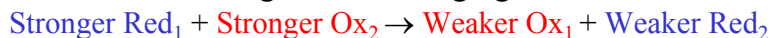
⇒ **Higher** (more positive)  $E^\circ$  means

- **Stronger oxidizing agent (Ox)** ← Ox is reduced
- **Weaker reducing agent (Red)** ← Red is oxidized

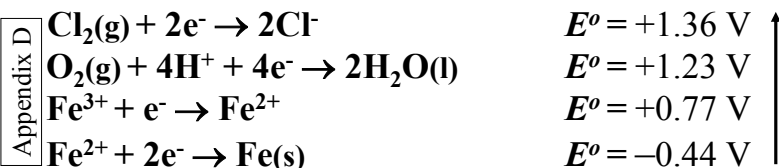
- **Electrochemical series** – an arrangement of the redox couples in order of decreasing reduction potentials ( $E^\circ$ ) → Appendix D
  - The most positive  $E^\circ$ s are at the top of the table
  - The most negative  $E^\circ$ s are at the bottom of the table
- ⇒ The **strongest oxidizing agents (Ox)** are **at the top** of the table **as reactants**
- ⇒ The **strongest reducing agents (Red)** are **at the bottom** of the table **as products**
- Every redox reaction is a sum of two half-reactions, one occurring as oxidation and another as reduction



- In a **spontaneous redox reaction**, the stronger oxidizing and reducing agents react to produce the weaker oxidizing and reducing agents



**Example:** Given the following half-reactions:



a) Rank the oxidizing and reducing agents by strength

→ Ox agents on the left; Red agents on the right

**Oxidizing** → (Top)  $\text{Cl}_2 > \text{O}_2 > \text{Fe}^{3+} > \text{Fe}^{2+}$  (Bottom)

**Reducing** → (Bottom)  $\text{Fe} > \text{Fe}^{2+} > \text{H}_2\text{O} > \text{Cl}^-$  (Top)

b) Can  $\text{Cl}_2$  oxidize  $\text{H}_2\text{O}$  to  $\text{O}_2$  in acidic solution?

→  $\text{Cl}_2/\text{Cl}^-$  has higher  $E^\circ$  ( $\text{Cl}_2/\text{Cl}^-$  is above  $\text{O}_2, \text{H}^+/\text{H}_2\text{O}$ )

⇒  $\text{Cl}_2$  is a stronger oxidizing agent than  $\text{O}_2$

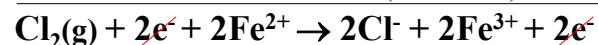
⇒  $\text{Cl}_2$  can oxidize  $\text{H}_2\text{O}$  to  $\text{O}_2$  at standard conditions

c) Write the spontaneous reaction between the  $\text{Cl}_2/\text{Cl}^-$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couples and calculate its  $E^\circ_{\text{cell}}$

→  $\text{Cl}_2/\text{Cl}^-$  has the higher reduction potential ( $E^\circ$ )

⇒  $\text{Cl}_2/\text{Cl}^-$  undergoes **reduction**

⇒  $\text{Fe}^{3+}/\text{Fe}^{2+}$  undergoes **oxidation** (reverse equation)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{anod}} = +1.36 - (+0.77) = +0.59 \text{ V}$$

d) Is the reaction of disproportionation (simultaneous oxidation and reduction) of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and  $\text{Fe}(\text{s})$  spontaneous at standard conditions?

→ Need the sign of  $E^\circ_{\text{cell}}$

⇒  $\text{Fe}^{2+}/\text{Fe}(\text{s})$  undergoes **reduction**

⇒  $\text{Fe}^{3+}/\text{Fe}^{2+}$  undergoes **oxidation** (reverse equation)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{anod}} = -0.44 - (+0.77) = -1.21 \text{ V}$$

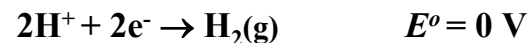
⇒  $E^\circ_{\text{cell}} < 0$  → the reaction is **non-spontaneous** at standard conditions

## Relative Reactivity of Metals

- The **activity series** of metals – ranks metals based on their ability to displace  $\text{H}_2$  from acids or water or displace each other's ions in solution

• **Metals that can displace  $\text{H}_2$  from acids**

– The reduction of  $\text{H}^+$  from acids to  $\text{H}_2$  is given by the standard hydrogen half-reaction



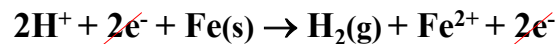
– In order for this half-reaction to proceed as written, the metal must have lower reduction potential (**the metal must be below  $\text{H}_2/\text{H}^+$**  in Appendix D)

⇒ If  $E^\circ_{\text{metal}} < 0$ , the metal **can** displace  $\text{H}_2$  from acids

⇒ If  $E^\circ_{\text{metal}} > 0$ , the metal **cannot** displace  $\text{H}_2$

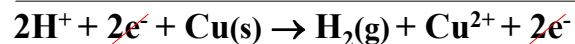
**Example:** Can Fe and Cu be dissolved in HCl(aq)?

→  $\text{Fe}^{2+}/\text{Fe}$  is below and  $\text{Cu}^{2+}/\text{Cu}$  is above  $\text{H}_2/\text{H}^+$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{anod}} = 0.00 - (-0.44) = +0.44 \text{ V}$$

⇒  $E^\circ_{\text{cell}} > 0$  → spontaneous (Fe dissolves in HCl)

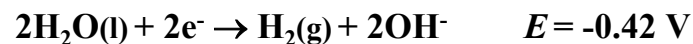


$$E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{anod}} = 0.00 - (+0.34) = -0.34 \text{ V}$$

⇒  $E^\circ_{\text{cell}} < 0$  → non-spontaneous (Cu doesn't dissolve)

• **Metals that can displace  $\text{H}_2$  from water**

– The reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  is given by:

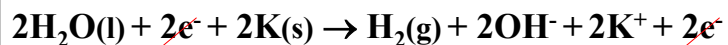


– The value of  $E$  is for  $\text{pH} = 7$  (nonstandard state)

⇒ Metals that are **below  $\text{H}_2\text{O}/\text{H}_2, \text{OH}^-$**  in Appendix D can displace  $\text{H}_2$  from water at standard conditions

⇒ Metals that have  $E^\circ_{\text{metal}} < -0.42$  can displace  $\text{H}_2$  from water at  $\text{pH} = 7$

**Example:** Potassium, **K**, dissolves readily in water



$$E^\circ_{\text{cell}} = -0.42 - (-2.93) = +2.51 \text{ V} > 0 \quad (\text{spontaneous})$$