

## Galvanic Cell Notation

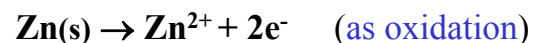
### • Half-cell notation

- Different phases are separated by vertical lines
- Species in the same phase are separated by commas

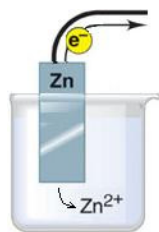
### • Types of electrodes

- **Active electrodes** – involved in the electrode half-reaction (most metal electrodes)

**Example:** Zn<sup>2+</sup>/Zn metal electrode



Notation:  $\text{Zn(s)} \mid \text{Zn}^{2+}$

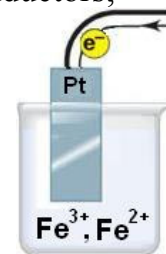


- **Inactive (inert) electrodes** – not involved in the electrode half-reaction (inert solid conductors; serve as a contact between the solution and the external el. circuit)

**Example:** Pt electrode in Fe<sup>3+</sup>/Fe<sup>2+</sup> soln.

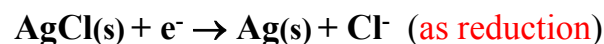


Notation:  $\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt(s)}$

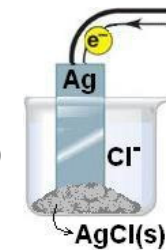


- Electrodes involving **metals** and their **slightly soluble salts**

**Example:** Ag/AgCl electrode

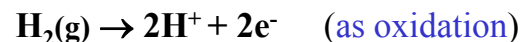


Notation:  $\text{Cl}^- \mid \text{AgCl(s)} \mid \text{Ag(s)}$

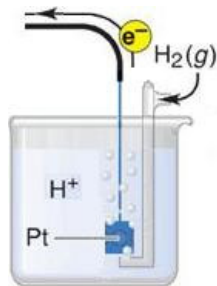


- Electrodes involving **gases** – a gas is bubbled over an inert electrode

**Example:** H<sub>2</sub> gas over Pt electrode



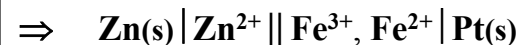
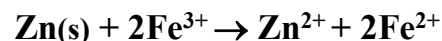
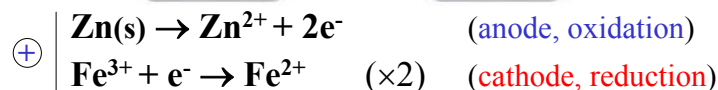
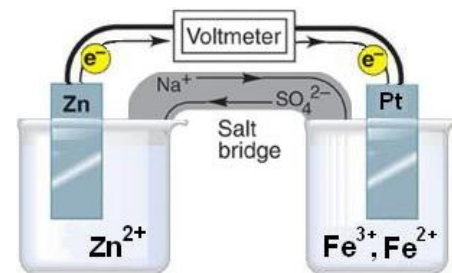
Notation:  $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{H}^+$



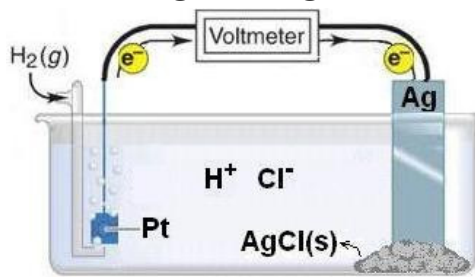
### • Cell notation

- The anode half-cell is written on the left of the cathode half-cell
- The electrodes appear on the far left (anode) and far right (cathode) of the notation
- Salt bridges are represented by double vertical lines

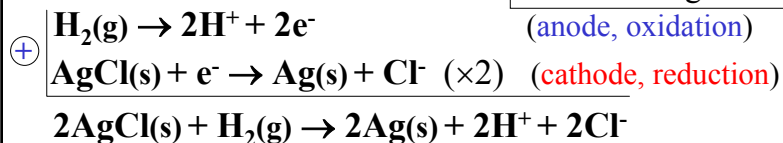
**Example:** A combination of the  $\text{Zn(s)} \mid \text{Zn}^{2+}$  and  $\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt(s)}$  half-cells leads to:



**Example:** A combination of the  $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+$  and  $\text{Cl}^- | \text{AgCl(s)} | \text{Ag(s)}$  half-cells leads to:

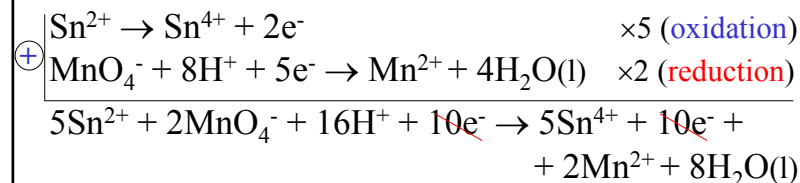


**Note:** The reactants in the overall reaction are in different phases (no physical contact)  $\Rightarrow$  no need of a salt bridge (anode, oxidation)



**Example:** Write the cell reaction and the cell notation for a cell consisting of a graphite cathode immersed in an acidic solution of  $\text{MnO}_4^-$  and  $\text{Mn}^{2+}$  and a graphite anode immersed in a solution of  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$ .

$\rightarrow$  Write the half reactions (a list of the most common half-reactions is given in **Appendix D**)



$\rightarrow$  The graphite (C) electrodes are inactive



## Why Do Galvanic Cells Work?

- Consider a cell made of two active metal electrodes,  $\text{M}_1$  and  $\text{M}_2$ , and their ions.
  - $\triangleright$  If the cell circuit is open, the two metals are in equilibrium with their ions
    - $\text{M}_1 \leftrightarrow \text{M}_1^+ + \text{e}^-$
    - $\text{M}_2 \leftrightarrow \text{M}_2^+ + \text{e}^-$
  - $\triangleright$  The produced electrons accumulate in the metal electrodes and produce **electrical potentials**
  - $\triangleright$  If  $\text{M}_1$  has a greater tendency to give out its electrons, the 1<sup>st</sup> equilibrium is shifted further to the right and the potential of  $\text{M}_1$  is more negative
  - $\triangleright$  When the circuit is closed, electrons flow from the more negative  $\text{M}_1$  (anode) toward the less negative  $\text{M}_2$  (cathode)

## 21.3 Cell Potentials

- Electromotive force (*emf*)** – drives the electrons in the el. circuit
  - $\text{emf}$  is the difference between the electrical potentials of the two electrodes (voltage)
- Cell potential ( $E_{\text{cell}}$ )**  $\rightarrow E_{\text{cell}} = \text{emf}$ 
  - Units  $\rightarrow$  volts (V)  $\rightarrow (1 \text{ V} = 1 \text{ J/C}$  since the electrical work is equal to the applied voltage times the charge moving between the electrodes)
- Standard cell potential ( $E_{\text{cell}}^\circ$ )** – the cell potential at standard-state conditions (gases  $\rightarrow$  1 atm, solutions  $\rightarrow$  1 M, liquids & solids  $\rightarrow$  pure)

➤  $E_{cell}$  is measured with a voltmeter

➤ If the (+) terminal of the voltmeter is connected to the (+) electrode (cathode), the voltmeter shows a positive reading

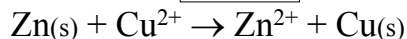
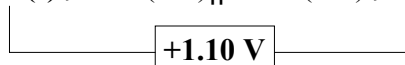
➤  $E_{cell}$  characterizes the overall cell reaction

➤ If  $E_{cell} > 0$ , the cell reaction is spontaneous

➤ If  $E_{cell} < 0$ , the cell reaction is non-spontaneous

➤ If  $E_{cell} = 0$ , the cell reaction is at equilibrium

**Example:**  $Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s)$



$E^o_{cell} = 1.10 \text{ V} > 0 \rightarrow$  spontaneous reaction

• **Electrode potentials ( $E$ )** – characterize the individual electrodes (half-reactions)

– The cell potential is the difference between the electrode potentials of the cathode and anode

$$E_{cell} = E_{cathode} - E_{anode}$$

• **Standard electrode potentials ( $E^o$ )** – electrode potentials at the standard-state

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

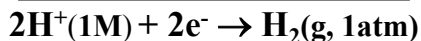
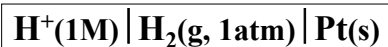
–  $E^o$  values are reported for the half-reaction written as reduction (**standard reduction potentials**) → listed in **Appendix D**

➤ Absolute values for  $E$  and  $E^o$  can't be measured

⇒ A **reference electrode** (half-cell) is needed

- The potentials of all electrodes are measured relative to the reference electrode

• **Standard hydrogen electrode** – used as a reference electrode →  $E^o_{ref} = 0 \text{ V}$  (assumed)



– To find the potential of any electrode, a cell is constructed between the unknown electrode and the reference electrode

– The cell potential is directly related to the unknown electrode potential

– If the unknown electrode is the cathode of the cell

$$\rightarrow E^o_{cell} = E^o_{unkn} - E^o_{ref}$$

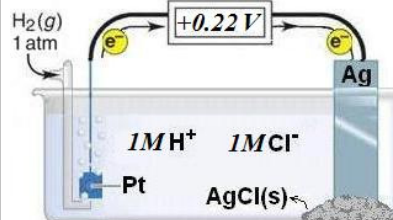
$$\rightarrow E^o_{unkn} = E^o_{cell} + E^o_{ref} = E^o_{cell} + 0 = E^o_{cell} > 0$$

– If the unknown electrode is the anode of the cell

$$\rightarrow E^o_{cell} = E^o_{ref} - E^o_{unkn}$$

$$\rightarrow E^o_{unkn} = E^o_{ref} - E^o_{cell} = 0 - E^o_{cell} = -E^o_{cell} < 0$$

**Example:**



$H^+/H_2 \rightarrow$  **anode**

$Ag/AgCl \rightarrow$  **cathode**

$$E^o_{cell} = E^o_{Ag/AgCl} - E^o_{ref} = E^o_{Ag/AgCl}$$

$$E^o_{Ag/AgCl} = +0.22 \text{ V}$$