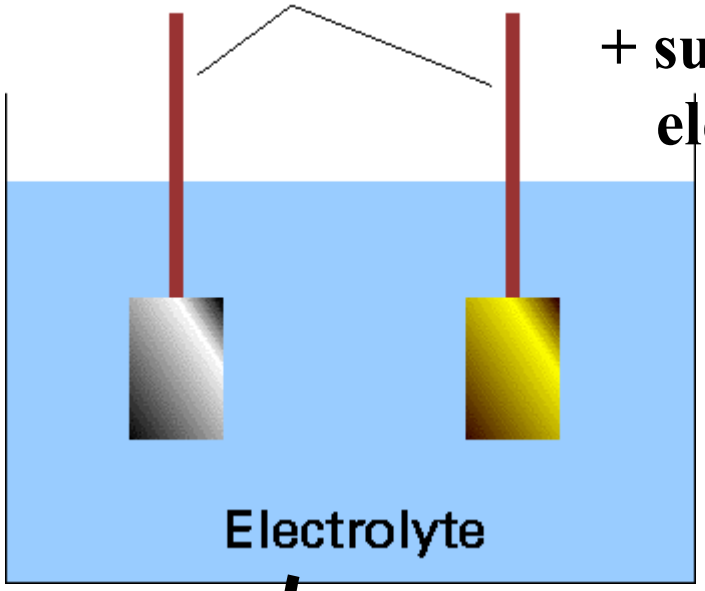
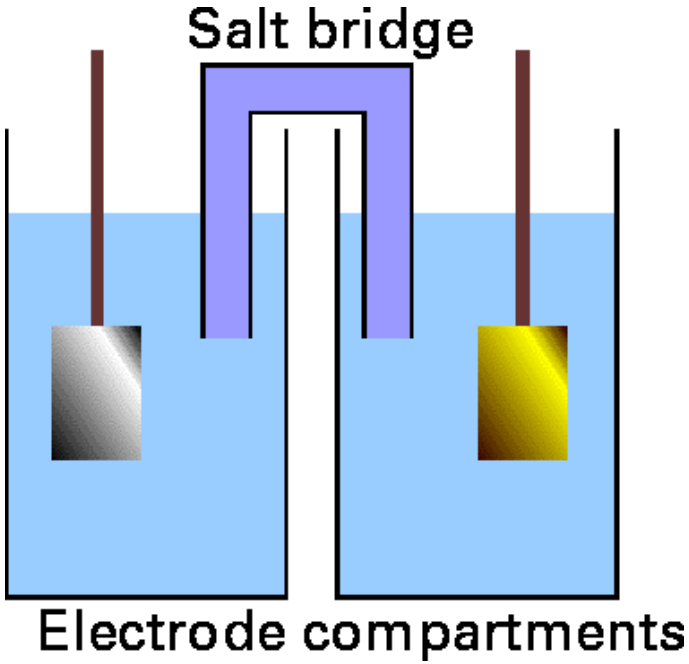
Electrochemical cells

Electrodes = electronic conductor + surrounding electrolyte



electrode compartment

If two different electrolytes are used:

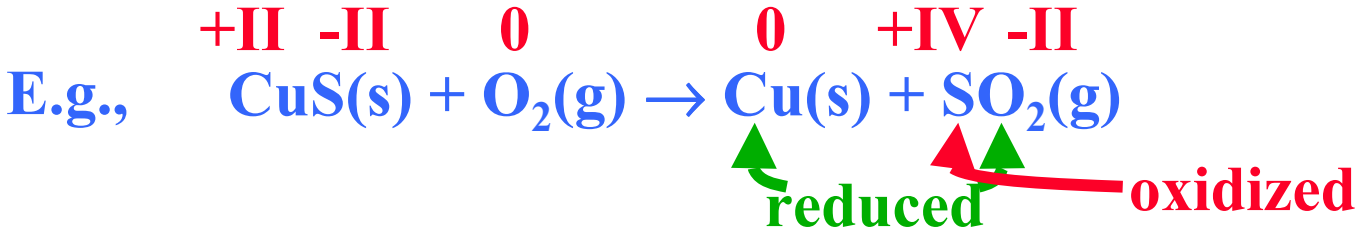


Galvanic cell: electrochemical cell in which electricity is produced as a result of a spontaneous reaction (e.g., batteries, fuel cells, electric fish!)

Electrolytic cell: electrochemical cell in which a non-spontaneous reaction is driven by an external source of current

Reactions at electrodes: Half-reactions

Redox reactions: Reactions in which electrons are transferred from one species to another



Any redox reactions can be expressed as the difference between two reduction half-reactions in which e^- are taken up

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

Reduction of Zn^{2+}: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

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

More complex: $MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Half-reactions are only a formal way of writing a redox reaction

Carrying the concept further

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

In general: redox couple Ox/Red, half-reaction Ox + νe^- → Red

Any reaction can be expressed in redox half-reactions:

$2\ H^+(aq) + 2e^- \rightarrow H_2(g, p_f)$

$2\ H^+(aq) + 2e^- \rightarrow H_2(g, p_i)$

Expansion of gas: $H_2(g, p_i) \rightarrow H_2(g, p_f)$

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

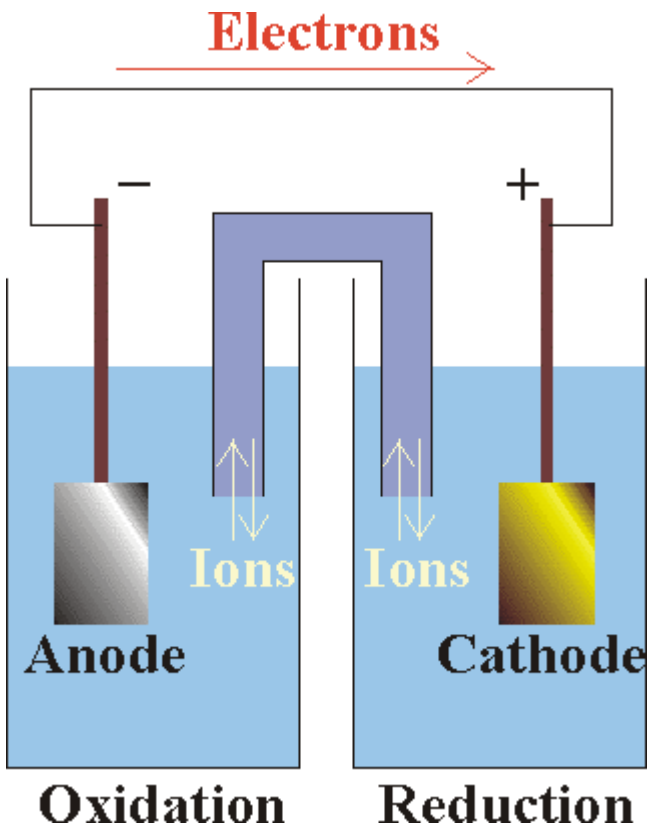
$Ag^+(aq) + e^- \rightarrow Ag(s)$

Dissolution of a sparingly soluble salt: $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

Reaction quotients: $Q = a_{Cl^-} \approx [Cl^-]$ $\quad Q = \dfrac{1}{a_{Ag^+}} \approx \dfrac{1}{[Ag^+]}$

Reactions at electrodes

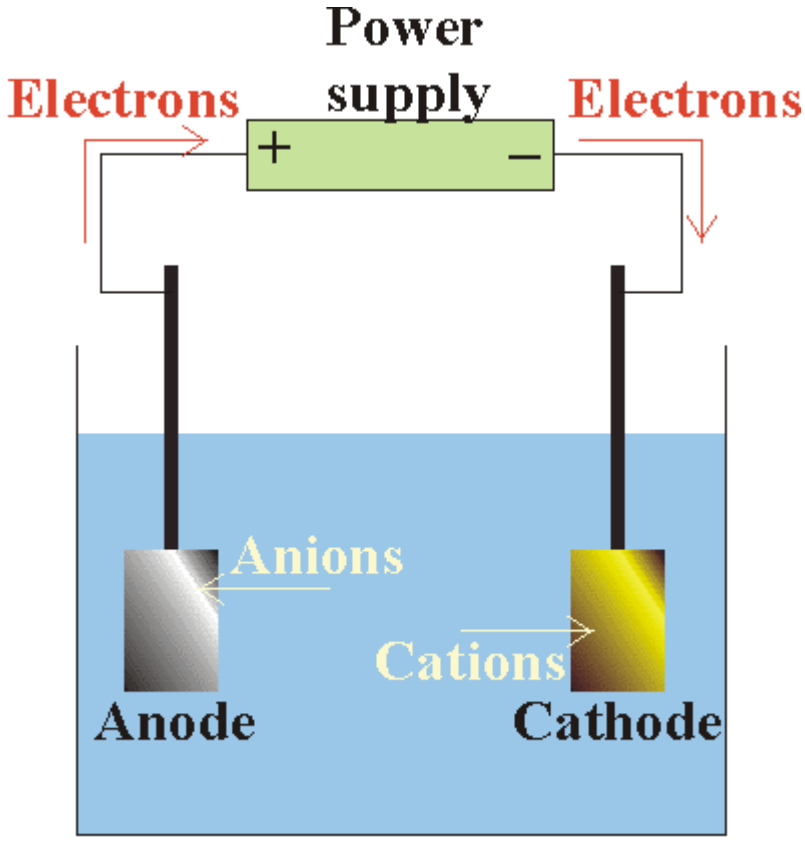
Galvanic cell:



$Red_1 \rightarrow Ox_1 + \nu e^-$

$Ox_2 + \nu e^- \rightarrow Red_2$

Electrolytic cell:



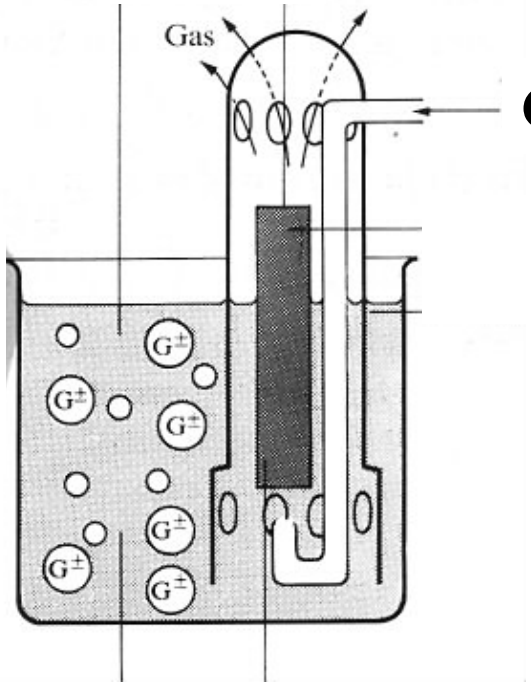
$Red_1 \rightarrow Ox_1 + \nu e^-$

$Ox_2 + \nu e^- \rightarrow Red_2$

Half-reactions

Types of electrodes I

Gas electrode:



Gas (e.g., H_2)

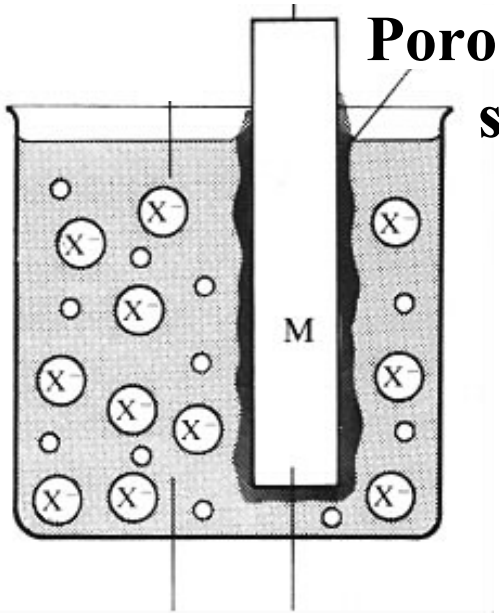
solution (e.g., H^+)

metal (e.g., Pt)

$Pt(s)|\ H_2(g)|\ H^+(aq)$

$2H^+ + 2e^- \rightleftharpoons H_2(g)$ $Q = \dfrac{p(H_2)}{a_{H^+}^{\ 2}}$

Insoluble-salt electrode:



Porous, insoluble salt (e.g., AgCl)

solution (e.g., Cl^-)

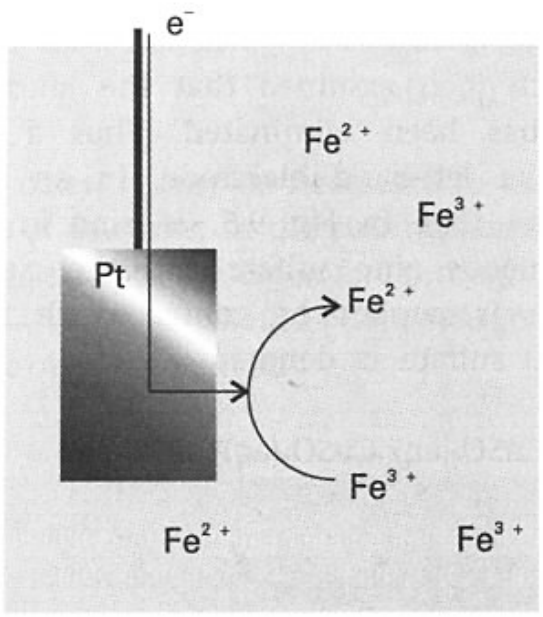
metal (e.g., Ag)

$Ag(s)|\ AgCl(s)|\ Cl^-(aq)$ $Q = a_{Cl^-}$

$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$

Types of electrodes and how to put them together in a galvanic cell

Redox electrode:

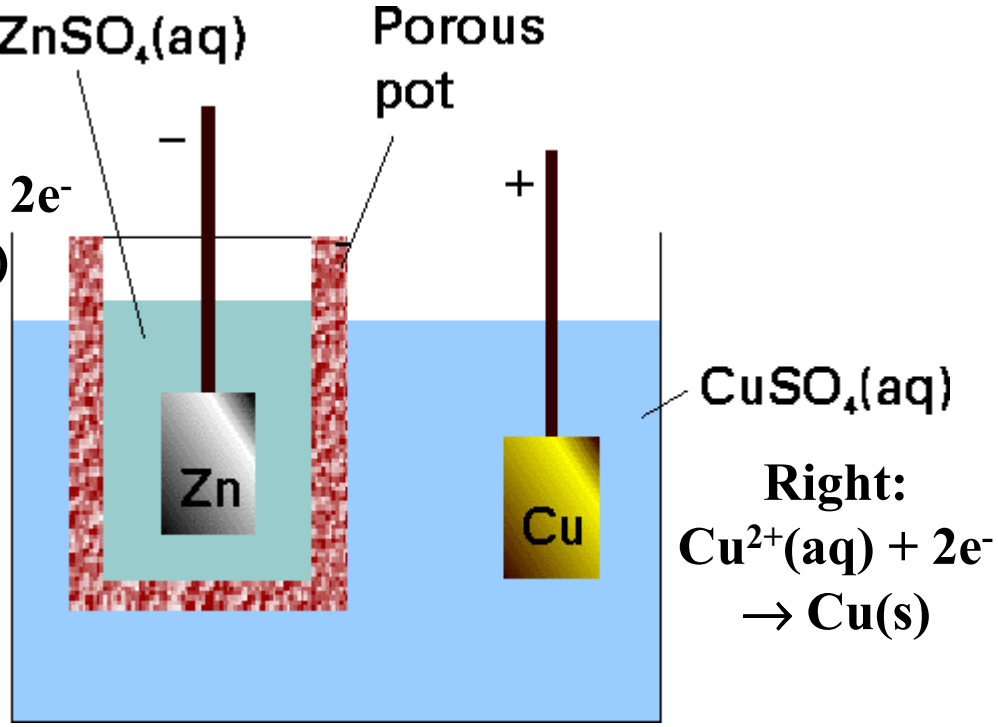


$Pt(s)|\ Fe^{2+}(aq), Fe^{3+}(aq)$

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

$$Q = \frac{a_{Red}}{a_{Ox}} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Daniell cell:



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

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

$$Q = \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

Cell reaction and potential

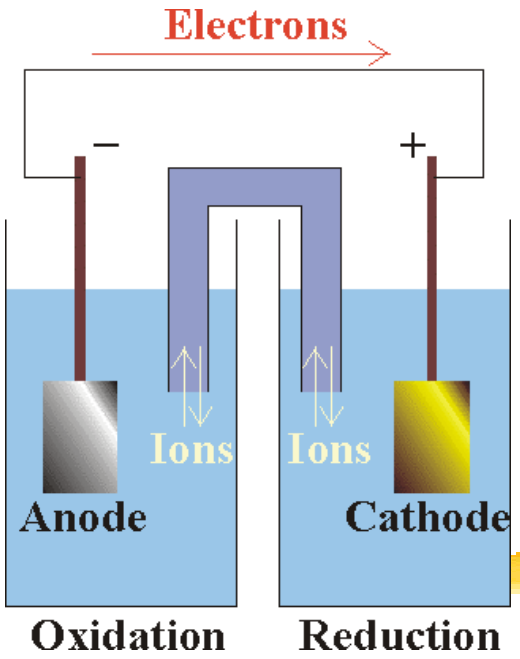
Cathode (Right): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (Left): $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

} this way the reaction becomes spontaneous

Overall (R-L): $Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$ ▶ e^- disappear

Cell reaction: Difference of electrode half-reactions (Reduction at Cathode - Oxidation at Anode)



Cell potential E: Potential difference between the electrodes

$Ox + \nu e^- \rightarrow Red \Rightarrow \nu N_A$ e^- transferred per mole of reaction

Faraday constant = eN_A = 96,485 $Cmol^{-1}$

$\Rightarrow \nu N_A \times (-e) = -\nu F$ charge transferred

Maximum electrical work done in a galvanic cell: $w' = -\nu F \times E = \Delta_r G$