

Spontaneity of Redox Reactions

**relationship between thermodynamics
and electrochemistry**

Cell potential, Electric work, Free energy

the work that can be accomplished when electrons are transferred through a wire depending on the “push” (volts i.e. EMF)

$$\text{volts} = \frac{1 \text{ Joule}}{1 \text{ coulomb}}$$

$$\varepsilon = \frac{-w}{q} \quad \text{thus} \quad w = -q \varepsilon$$

Cell potential, Electric work, Free energy

the work that can be accomplished when electrons are transferred through a wire depends on the “push” (volts i.e. EMF)

the minus sign represents electrical energy leaving the system

$$\varepsilon = \frac{-w}{q} \quad \text{thus} \quad w = -q\varepsilon$$

Cell potential, Electric work, Free energy

**1 mol of electrons has a charge of 96485
Coulombs**

= 1 Faraday (f)

$$w = \Delta G = -q\varepsilon$$

$$\Delta G = -q\varepsilon = -n f \varepsilon$$

$$\text{and } \Delta G^\circ = -n f \varepsilon^\circ$$

**the cell potential is directly related to the Free
Energy difference between reactants and
products**

Cell potential, Electric work, Free energy

ΔG is negative when ε is positive; the reaction is spontaneous

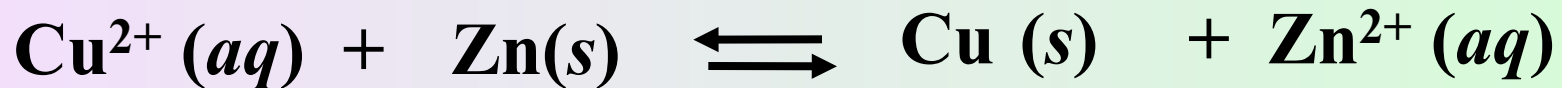
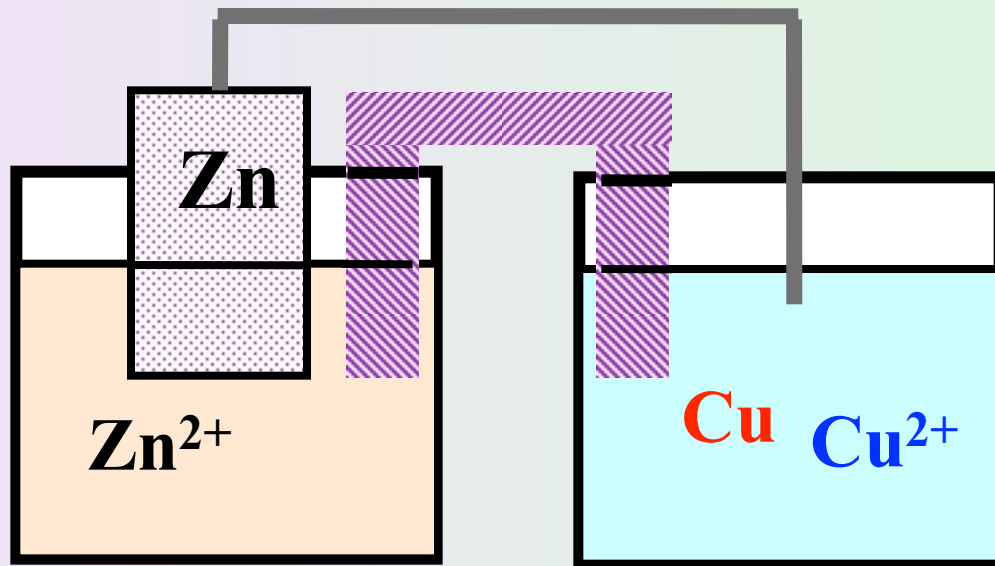
$$\Delta G^\circ = -n f \varepsilon^\circ = -RT \ln K$$

at 25 ° C:

$$\varepsilon^\circ = \frac{0.0592}{n} \log K$$

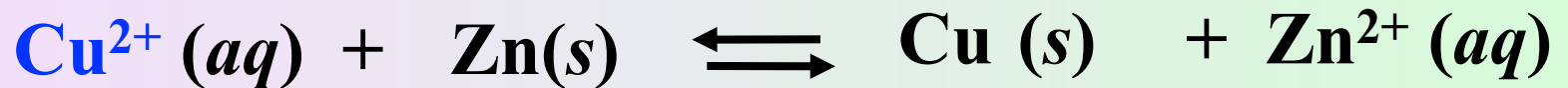
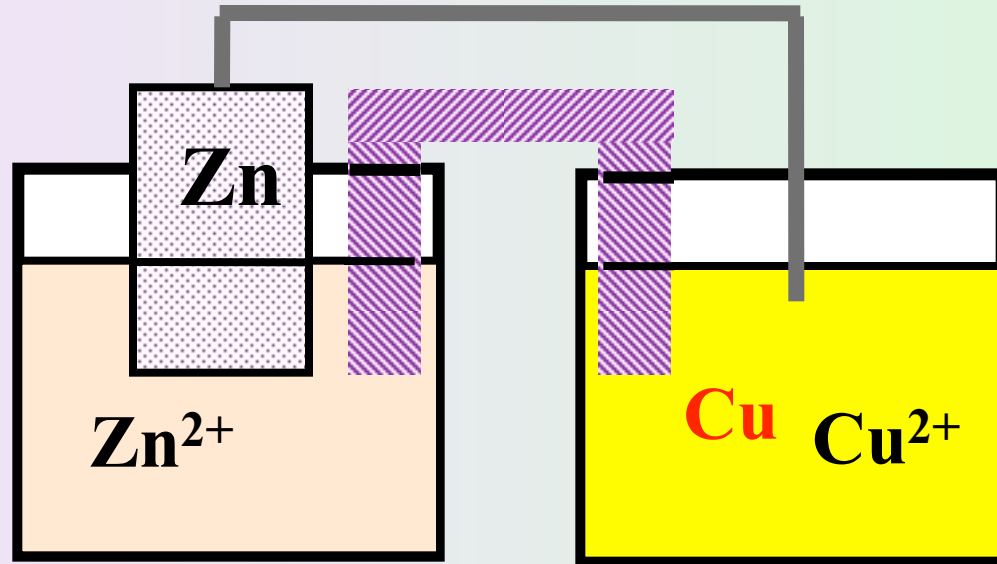
The Effect of Concentration on Cell EMF

Cell potential and concentration



Cell potential and concentration

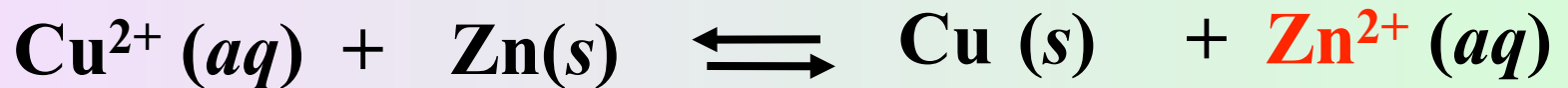
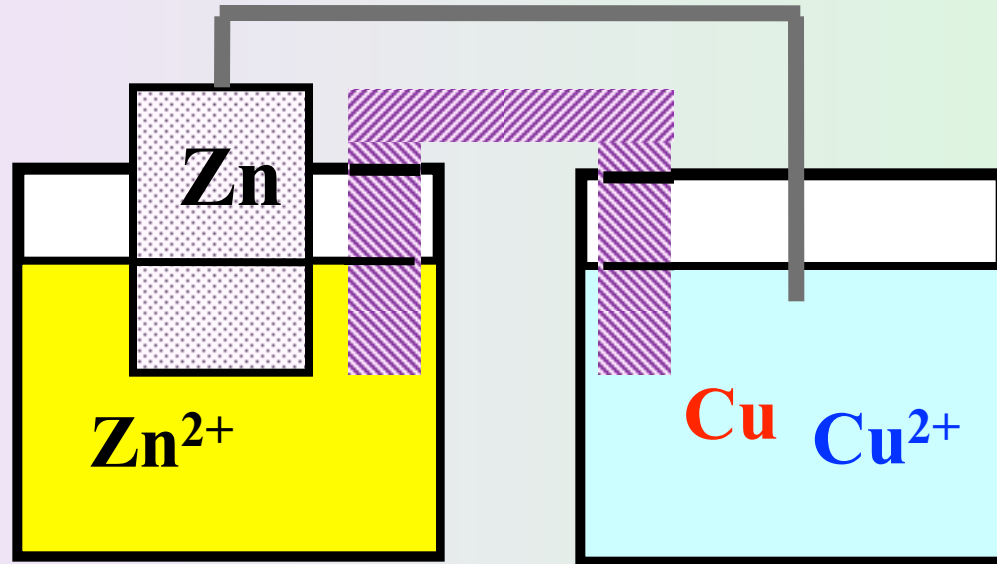
Le Chatelier's principle



Increasing the concentration of Cu^{2+} drives the reaction forward

Cell potential and concentration

Le Chatelier's principle



Increasing the concentration of **Zn²⁺** impedes the forward reaction

Cell potential and concentration

the dependence of the cell potential on concentration results directly from the dependence of free energy on concentration

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$

The Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln (Q) \quad \Delta G^\circ = -n f \varepsilon^\circ$$

$$\Delta G = -n f \varepsilon$$

$$-n f \varepsilon = -n f \varepsilon^\circ + RT \ln (Q)$$

$$\varepsilon = \varepsilon^\circ - \frac{RT}{n f} \ln (Q)$$

at 25 ° C:

$$\varepsilon = \varepsilon^\circ - \frac{0.0592}{n} \log (Q)$$

The Nernst Equation

$$\varepsilon = \varepsilon^{\circ} - \frac{0.0592}{n} \log (Q)$$

at equilibrium

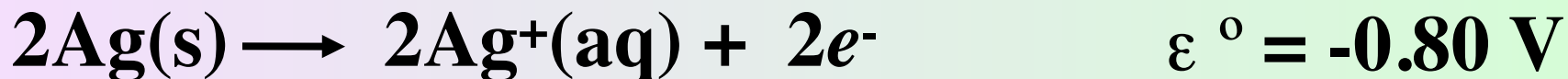
$$\varepsilon = 0$$

$$Q = K$$

$$\varepsilon^{\circ} = \frac{0.0592}{n} \log K$$

Practice Exercise

What is K for the reaction shown at 25 °C?



$$\varepsilon^{\circ} = -1.24 \text{ V}$$



$$\varepsilon^{\circ} = -1.24 \text{ V}$$

$$\varepsilon = \varepsilon^{\circ} - \frac{0.0592}{n} \log Q$$

at equilibrium:

$$0 = -1.24 - \frac{0.0592}{2} \log K$$

$$\log K = - \frac{2 \times 1.24}{0.0592} = -41.9 \quad \mathbf{K = 1.3 \times 10^{-42}}$$

Example

Is the reaction spontaneous at 25 °C?



0.60 M

0.01 M



$$\varepsilon = \varepsilon^{\circ} - \frac{0.0592}{n} \log(Q) \quad \varepsilon^{\circ} = -0.04 \text{ V}$$

$$\varepsilon = -0.04 \text{ V} - \frac{0.0592}{2} \log \frac{0.01}{0.60}$$

$$\varepsilon = -0.04 \text{ V} - (-0.05 \text{ V}) = \mathbf{+0.01 \text{ V}}$$

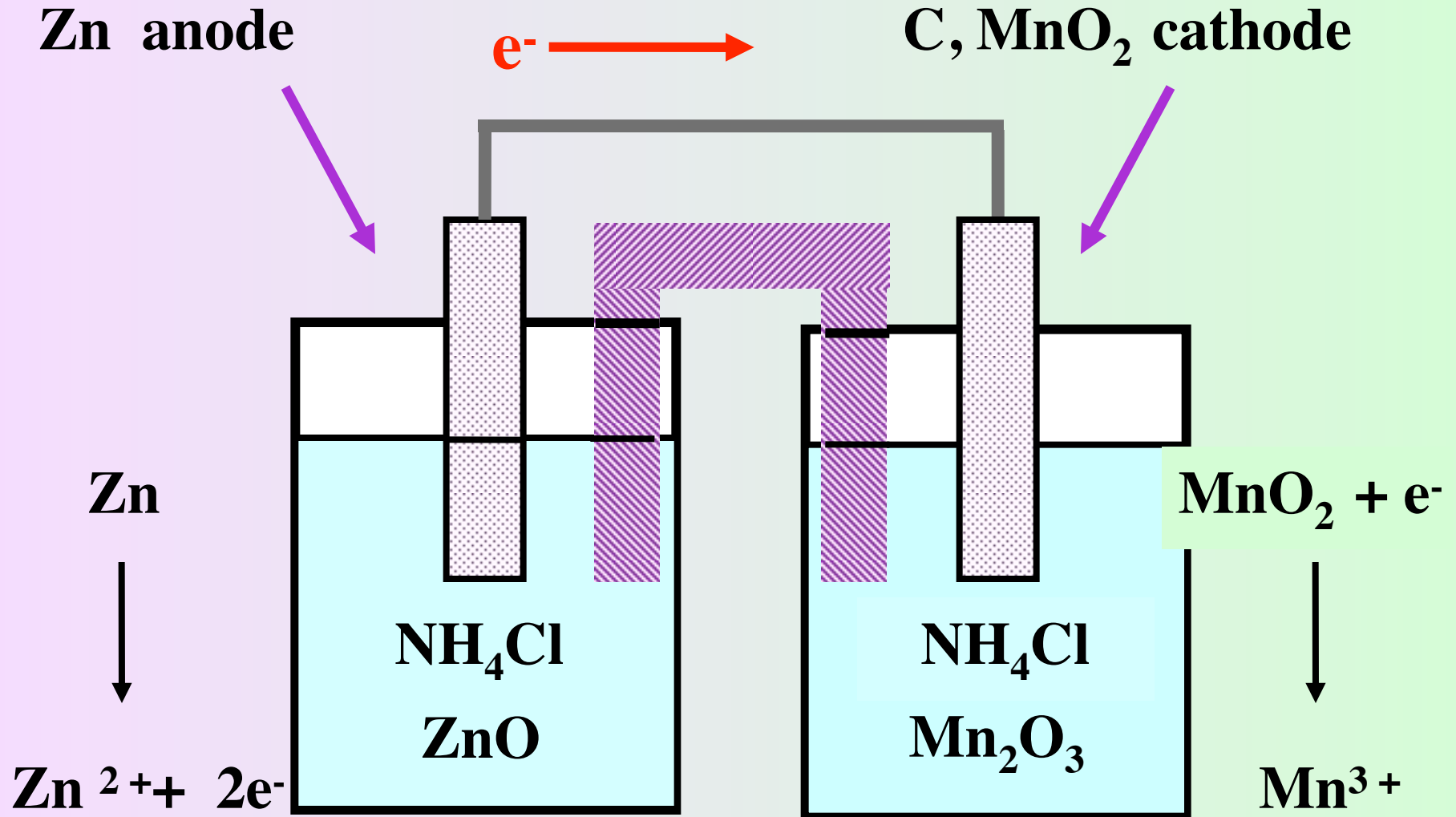
Batteries

Batteries

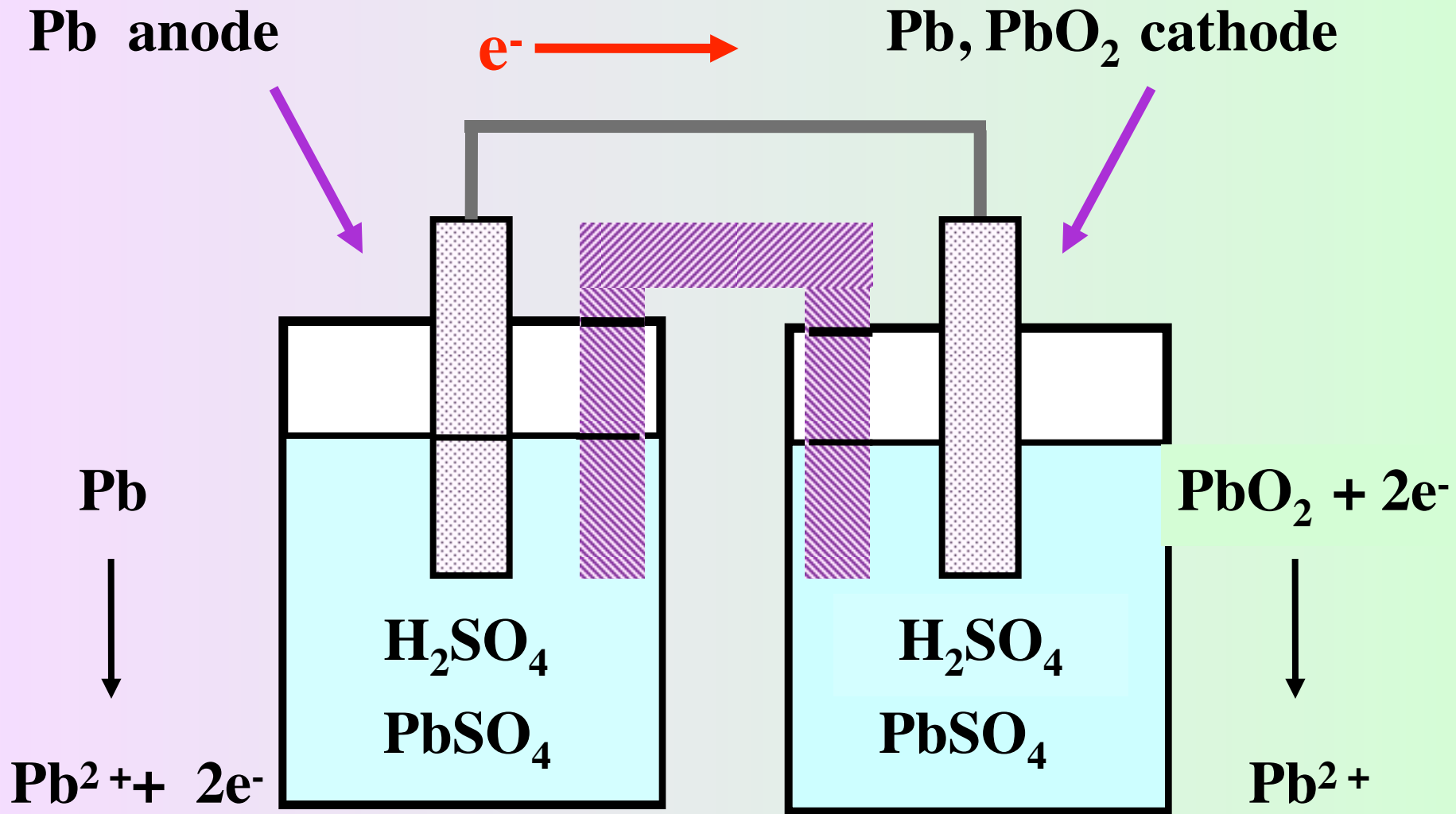
a galvanic cell

the voltage is the sum of individual cell voltages for group of galvanic cells connected in series

Dry Cell Battery



Lead Storage Battery



Fuel Cells

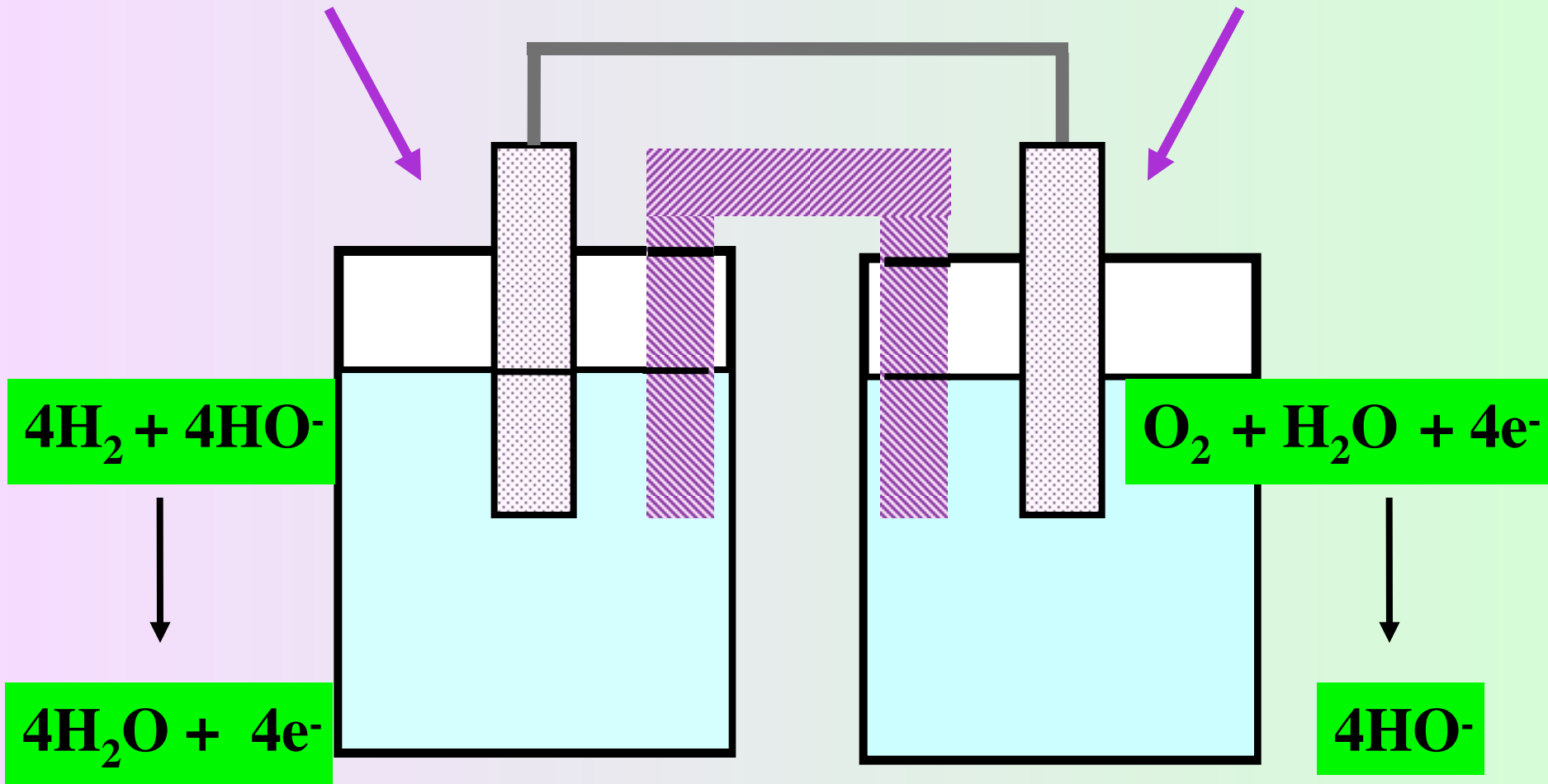
a galvanic cells for which the reactants are continuously supplied

Hydrogen-Oxygen Fuel Cell

C anode

C cathode

e^- →



Hydrogen-Oxygen Fuel Cell

C anode

C cathode

e^- →

