

# NERNST EQUATION

- The cell potential of a galvanic cell depends on the concentrations of the reactants and products of the cell reaction.
- The cell potential generated under **non-standard conditions** can be calculated using **Nernst equation**.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

**where**


**Q** = reaction quotient

**n** = number of moles of  $e^{-}$

# Nernst Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log Q$$


$$\frac{2.303 (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (298.15 \text{ K})}{n(96495 \text{ J V}^{-1} \text{ mol}^{-1})} \log Q$$

**At 25 °C**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

- The Nernst equation for the general equation :



At 25 °C

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q



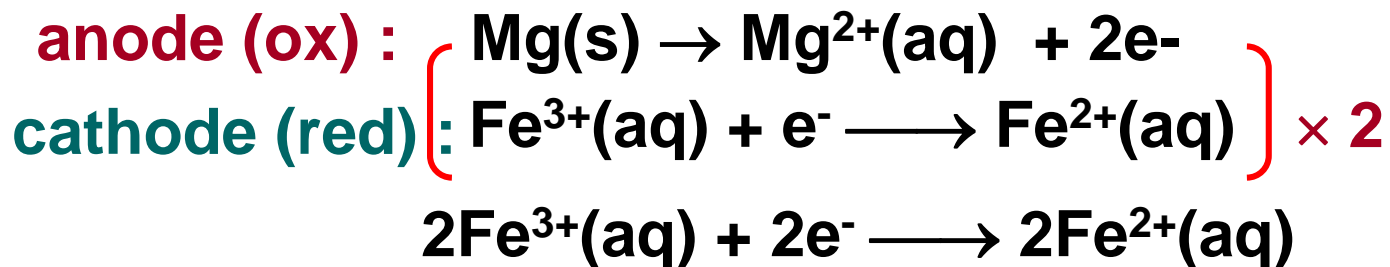
- Only species with concentration or partial pressure are included Q expression.  
**Solid and liquid are excluded.**
- $E_{\text{cell}}$  could be **increased by decreasing the Q**, this can be done by
  - ▶▶ **Increasing the concentration of reactant or**
  - ▶▶ **Decreasing the concentration of product**

# Uses of Nernst equation

- ✓ To calculate  $E_{\text{cell}}$  at non-standard condition.
- ✓ To predict spontaneity of a cell reaction at non-standard condition.
- ✓ To calculate concentration of ions or partial pressure of a gas in a galvanic cell at non-standard condition.
- ✓ To determine equilibrium constant,  $K$ .

# Determination of $E_{\text{cell}}$ and predict spontaneity of a cell reaction at non-standard condition

## Example



Nernst equation :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$n = 2$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{Mg}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{\text{Mg}/\text{Mg}^{2+}} \\ &= +0.77 - (-2.37) \\ &= +3.14 \text{ V} \end{aligned}$$

**Nernst equation :**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{Mg}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

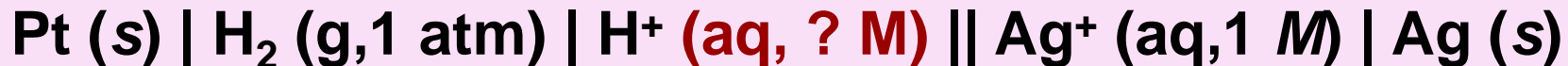
$$\begin{aligned} E_{\text{cell}} &= 3.14 - \frac{0.0592}{2} \log \frac{(10.0)(1.0)^2}{(5.0)^2} \\ &= +3.153 \text{ V} \end{aligned}$$

$$E_{\text{cell}} > 0$$

**∴ The reaction occurs spontaneously.**

# Determination of Ion Concentration

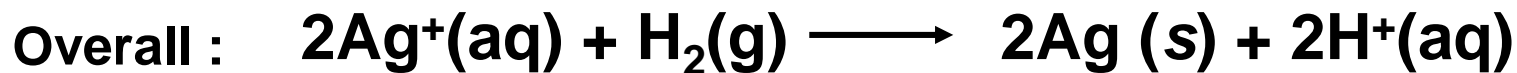
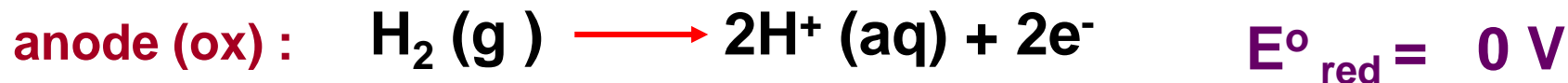
## Example



$$E_{\text{cell}} = + 0.98 \text{ V} \quad \text{at } 298 \text{ K}$$

Determine the  $\text{H}^+$  ions concentration, and the pH of  $\text{H}^+$  solution in the galvanic cell.

### Solution :



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = + 0.80 - 0.00 = +0.80 \text{ V}$$

## Nernst equation :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

$$0.98 = 0.80 - \frac{0.0592}{2} \log \frac{[\text{H}^+]^2}{(1)^2 (1)}$$

$$\log \frac{[\text{H}^+]^2}{(1)^2 (1)} = (0.80 - 0.98) \times \frac{2}{0.0592}$$

$$\log[\text{H}^+]^2 = -6.081$$

$$2\log[\text{H}^+] = -6.081$$

$$\log[\text{H}^+] = -3.041$$

$$\text{pH} = -\log[\text{H}^+]$$

$$= -(-3.041)$$

$$= 3.041 //$$

$$[\text{H}^+] = \text{antilog}(-3.041) = 9.109 \times 10^{-4} \text{ M} //$$





# Determination of Equilibrium Constant , K



- As reactions proceed concentrations of products increase and reactants decrease.
- When the reactions reach **equilibrium**, no net reactions occur  $\Rightarrow Q = K$  and  $E_{\text{cell}} = 0$ ,

*Nernst*

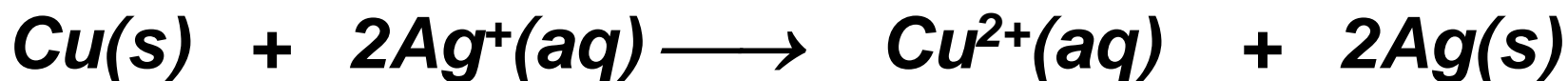
*equation :* 
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$0 = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log K$$

$$E^{\circ}_{\text{cell}} = \frac{0.0592}{2} \log K$$

## Example

Calculate the equilibrium constant (K) for the following reaction.



**Solution :**

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$= E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$$

$$= + 0.80 - 0.34$$

$$= + 0.46 \text{ V}$$

At equilibrium,  $E_{\text{cell}} = 0$ ,  $Q = K$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$0 = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log K$$

$$E^{\circ}_{\text{cell}} = \frac{0.0592}{2} \log K$$

$$0.46 = \frac{0.0592}{2} \log K$$

$$\log K = 15.54$$

$$K = 3.467 \times 10^{15}$$