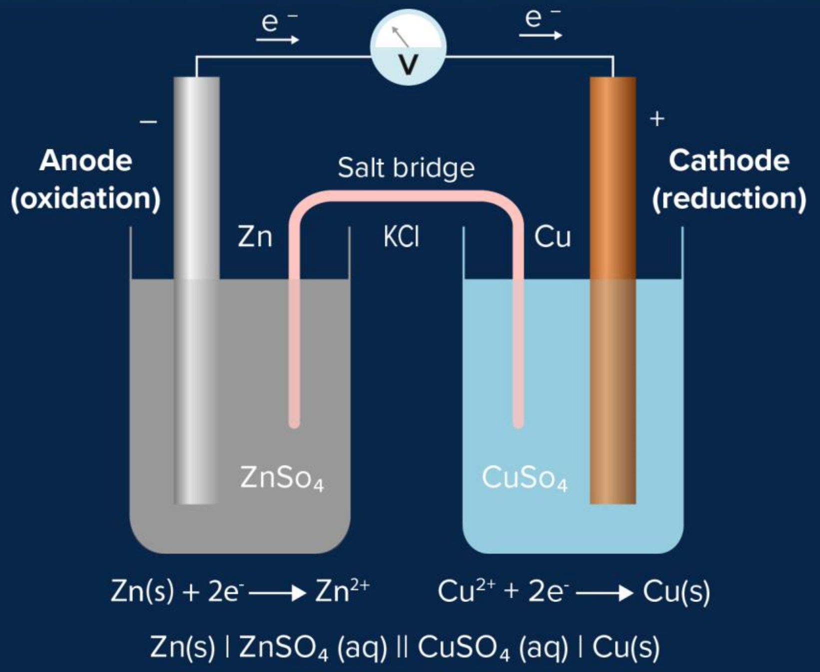
ELECTROCHEMISTRY- L5



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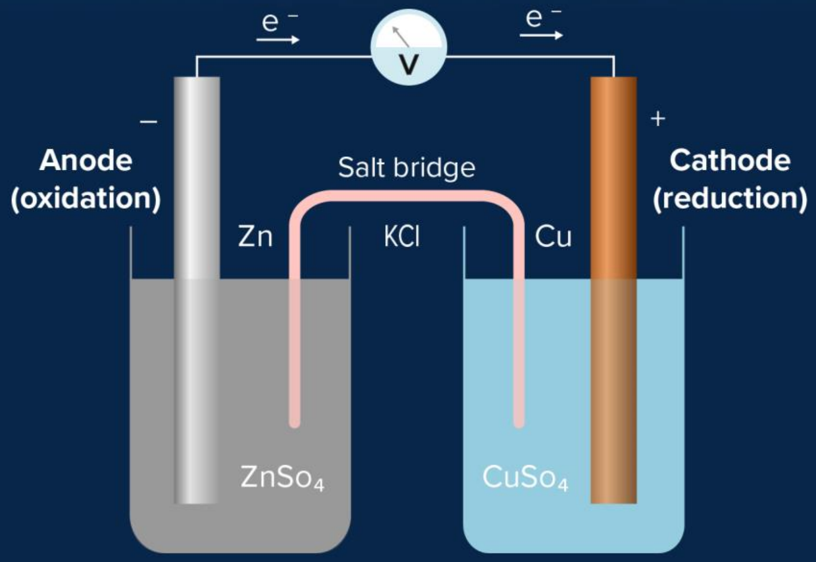
ELECTROCHEMISTRY- L5



$Zn(s) + 2e^- \longrightarrow Zn^{2+}$ $\quad$ $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

$Zn(s) \mid ZnSO_4\,(aq) \parallel CuSO_4\,(aq) \mid Cu(s)$

CHEMISTRY

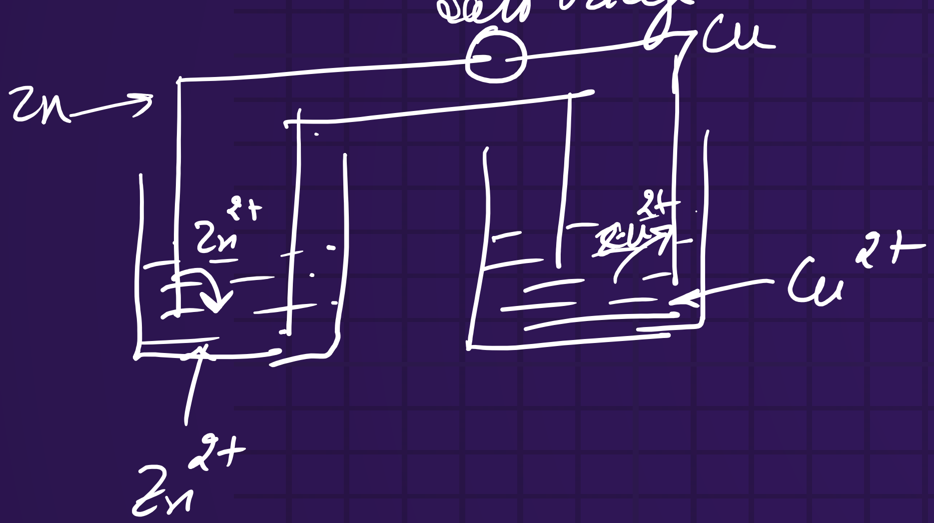
ANOOP SIR

Nernst Equation

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$

C_1 C_2

salt bridge



$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= E^\circ_{reduction} - E^\circ_{oxidation}$

$= E^\circ_{right} - E^\circ_{left}$

298 K Tells us the flow of positive charge in the cell

$E^\circ_{Zn^{2+}/Zn} = -0.76\,V$

$E^\circ_{Cu^{2+}/Cu} = +0.34\,V$

$E^\circ_{cell} = +0.34 - (-0.76)$

$= +0.34 + 0.76$

$= 1.1\,V$

For a cell to actually work, electrode with more positive reduction potential is the cathode (less negative)

Nernst Equation

Nernst equation is used to obtermine the cell or electrode potential at different concentrations or partial pressures.

$$E = E^{\circ} - \frac{2.303\,RT}{nF}\log Q$$

E = cell or electrode potential

E° = standard cell or electrode potential

R = gas constant ($8.314\ JK^{-1}mol^{-1}$)

T = Temperature → 298 K

F = Faraday → 96487 C ≈ 96500 C

$\frac{2.303\,RT}{F}$ = constant

0.0591 V

Nernst Equation

At 298 K

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

n & Q change with balancing of equation.

n = Electrons involved → accepted or released in the balanced electrode or cell reaction → n changes with how the equation is balanced.

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$ $n = 1$ $Q = \frac{(p_{H_2})^{1/2}}{[H^+]}$

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $n = 2$ $Q = \frac{p_{H_2}}{[H^+]^2}$ st coef

Q = Reaction quotient = $\frac{[\text{Product}]}{[\text{Reactants}]}$ st. coef.

Nernst Equation

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$ 298K

0.1M 0.001M

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ $\rightarrow n = 2$

Reactant Product

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

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$$

$$= +0.34V - (-0.76V)$$

$$= +1.1V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.1V - \frac{0.0591}{2} V \log \frac{(0.1)}{(0.001)}$$

$$= 1.1 - \frac{0.0591}{2} \log(100) = \left(1.1 - \frac{0.0591}{2} \times 2\right) V$$

$$= 1.0409 V$$

Nernst Equation

$Zn_{(s)} | Zn^{2+}_{(aq)} \;(0.001M) \;||\; Cu^{2+} \;(0.1M) \;| Cu_{(s)}$ 298K

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

$$E_{cell} = 1.1V - \frac{0.0591}{2} \log \frac{(0.001)}{(0.1)}$$

$$= 1.1V - \frac{0.0591}{2} \log \frac{1}{100}$$

$$1.1 - \frac{0.0591}{2} \log 10^{-2}$$

$$1.1 - \frac{0.0591}{2} \times (-2) = 1.1 + 0.0591$$

$$= 1.1591 V$$

Increasing the concentration of product or decreasing the concentration of reactant decreases the cell potential.

Nernst Equation

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$ 298 K

1M $C_{Cu^{2+}}$

What should be the concentration of Cu^{2+} so that cell is at equilibrium.

Ans. At equilibrium, $E_{cell} = 0\,V$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$0 = 1.1\,V - \frac{0.0591}{2} \log \frac{1\,M}{[Cu^{2+}]}$$

$$2.2\,V = 0.0591 \log \frac{1}{[Cu^{2+}]}$$

$$\log \frac{1}{[Cu^{2+}]} = \frac{2.2}{0.0591}$$

$$\log \frac{1}{[Cu^{2+}]} = -\log [Cu^{2+}]$$

$$-\log [Cu^{2+}] = 37.2$$

$$\log [Cu^{2+}] = -37.2$$

$$[Cu^{2+}] = 10^{-37.2}$$

Nernst Equation

$Cu_{(s)} | Cu^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$ 298K

0.001M (oxidation ↑ Product) 0.1M (↑ reduction, Reactant)

$E^{\circ}_{cell} = E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Cu^{2+}/Cu}$
$= 0V$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{(0.001M)}{(0.1)M}$$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \frac{1}{100}$$

$$E_{cell} = -\frac{0.0591}{2} \times (-2) V = +0.0591 V$$

Nernst Equation

Concentration cell → A cell which as 0 V standard potential as cathode and anode have same reduction reaction but the cell still has a positive potential and works due to the difference in concentration (partial pressure) is termed concentration cell.

Nernst Equation

Factors Affecting Cell Potential

(1) **Temperature**

(2) **Composition** of the reaction mixtures

(3) **Partial pressure** of the gas (if any)

Nernst Equation

The dependence
of the concentration and
pressure of the gas
on the cell potential
can be derived from
thermodynamics.

Nernst Equation for Half-Cells

Metal–Metal Soluble Salt Electrode

Considering a half-cell reaction,

$$M^{n+} (aq) + ne^{-} \longrightarrow M (s)$$

Cell representation

$M^{n+} (aq) \mid M (s)$

Nernst Equation

We know, for any reaction,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q$$

$$-nFE = -nFE^0 + 2.303\ RT \log Q$$

Q - Reaction quotient

Metal–Metal Soluble Salt Electrode

Nernst equation for the half-cell,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$= E^0_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

Metal–Metal Soluble Salt Electrode

Similarly, for oxidation,

$$B(s) \longrightarrow B^{m+}(aq) + me^-$$

$$E_{B/B^{m+}} = E^0_{B/B^{m+}} - \frac{2.303RT}{mF}\log\,[B^{m+}(aq)]$$

Cell representation: **B (s) | B^{m+} (aq)**

Metal–Metal Soluble Salt Electrode

Example

Zinc half-cell

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$$

Electrode potential

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

Cell representation: **Zn^{2+} (aq) | Zn (s)**

Metal–Metal Soluble Salt Electrode

Other **examples:**

Cu^{2+}/Cu, Ag^{+}/Ag, etc.

Nernst Equation for Cell potential

Nernst Equation

For any reaction,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q$$

$$-nFE_{cell} = -nFE^0_{cell} + 2.303\, RT \log Q$$

Q - Reaction quotient

Reaction Quotient

For any reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad ...(1)$$

Nernst Equation

$$E_{cell} = E^0_{cell} - \frac{2.303\ RT}{nF} \log Q \quad ...(2)$$

Nernst equation

Where,
R = Universal gas constant
T = Temperature
n = Number of transferred electrons
F = Faraday's constant
Q = Reaction quotient

Nernst Equation

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \quad \ldots(1)$$

Putting the value of eq. 1 in eq. 2,

$$E_{cell} = E^0_{cell} - \frac{2.303\,RT}{nF} \log \frac{[C]^c}{[D]^d}$$

$[A]^a$

$[B]^b$

Nernst Equation

Take

T = 298 K
R = 8.314 J/mol K
F = 96500 C/mol

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log Q$$

$$= E^0_{cell} - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be:

0.15 + 0.74

AIPMT 2011

a) +1.19 V

b) +0.89 V

c) +0.18 V

d) +1.83 V

Consider the following relations for emf of an electrochemical cell:

(i) EMF of cell = (Oxidation potential of anode) – (Reduction potential of cathode)

(ii) EMF of cell = (Oxidation potential of anode) + (Reduction potential of cathode)

(iii) EMF of cell = (Reduction potential of anode) + (Reduction potential of cathode)

(iv) EMF of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

AIPMT 2010

Which of the given relations are correct?

AIPMT 2010

a. (iii) and (i)

b. (i) and (ii)

c. (iii) and (iv)

d. (ii) and (iv)

In the electrochemical cell

$Zn \mid ZnSO_4$ (0.01 M) || $CuSO_4$ (1.0 M) | Cu, the emf of this Daniel cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0 M, the emf changes to E_2. From the following, which one is the relationship between E_1 and E_2? (Given, RT/F = 0.059)

NEET 2017

a. $E_1 < E_2$

b. $E_1 > E_2$

c. $E_1 = 0^1E_2$

d. $E_1 = E_2$

Given: Zn | $ZnSO_4$ (0.01 M) || $CuSO_4$ (1.0 M) | Cu; E_1

Zn | $ZnSO_4$ (1 M) || $CuSO_4$ (1.0 M) | Cu; E_2

To find: Relationship between E_1 and E_2

For the electrochemical cell,

Mg (s) | Mg^{2+} (aq, 1 M) || Cu^{2+} (aq, 1 M) | Cu (s), the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. Find the value of 'x'.

[Given, F/R = 11500 K V^{-1}, where F is Faraday's constant, R is gas constant, ln(10) = 2.30]

a 5

b 10

For the electrochemical cell,

$Mg\ (s)\ |\ Mg^{2+}\ (aq,\ 1\ M)\ ||\ Cu^{2+}\ (aq,\ 1\ M)\ |\ Cu\ (s)$, the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. Find the value of 'x'.

[Given, F/R = 11500 K V^{-1}, where F is Faraday's constant, R is gas constant, ln(10) = 2.30]

c 15

d 20

Given: Mg (s) | Mg^{2+} (aq, 1 M) || Cu^{2+} (aq, 1 M) | Cu (s)

$[Mg^{2+}]$ = 1 M: ${}_{0}E_{cell}$ = 2.70 V at 300 K, $[Mg^{2+}]$ = x M: E_{cell} = 2.67 V at 300 K,

F/R = 11500 K V^{-1}, ln(10) = 2.30

To find: x

Equilibrium in Electrochemical Cell

Equilibrium in Electrochemical Cell

From thermodynamics,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q$$

At **chemical equilibrium**,

$$\Delta_r G = 0$$

$$E_{cell} = 0$$

Cell will be of **no use**

Equilibrium in Electrochemical Cell

$$\Delta_r G^0 = -RT \ln K_{eq}$$

$$-nFE^0_{cell} = -2.303\ RT \log (K_{eq})$$

$$E^0_{cell} = \frac{2.303\ RT}{nF} \log K_{eq}$$

Equilibrium in Electrochemical Cell

$$\log K_{eq} = \frac{nF}{2.303\ RT} E^0_{cell}$$

Take **T** = 298 K, **R** = 8.314 J/mol K, **F** = 96500 C

$$\log K_{eq} = \frac{n}{0.059} E^0_{cell}$$

Given: $Hg_2^{2+} + 2e^- \longrightarrow 2Hg$, $E^0 = 0.789$ V and $Hg^{2+} + 2e^- \longrightarrow Hg$, $E^0 = 0.854$ V. Calculate the equilibrium constant for $Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$

a. 3.13×10^{-3}

b. 3.13×10^{-4}

c. 6.23×10^{-3}

d. 6.26×10^{-4}

Zn^{2+} (aq) + 4OH$^-$ (aq) $\longrightarrow$ $Zn(OH)_4^{2-}$ (aq); Value of equilibrium constant (K_f) for the given reaction is 10^x then find x.

Given: Zn^{2+} (aq) + 2e$^-$ $\longrightarrow$ Zn (s); $E^0 = 0.76$ V

$Zn(OH)_4^{2-}$ (aq) + 2e$^-$ $\longrightarrow$ Zn (s) + 4OH$^-$ (aq);

$$E^0 = -1.36 \text{ V}; \; 2.303 \frac{RT}{F} = 0.06$$

a	18
b	10
c	25
d	20

"Stay Positive, Work Hard. Make It Happen!"

THANK YOU