SNS COLLEGE OF TECHNOLOGY

AN AUTONOMOUS INSTITUTION

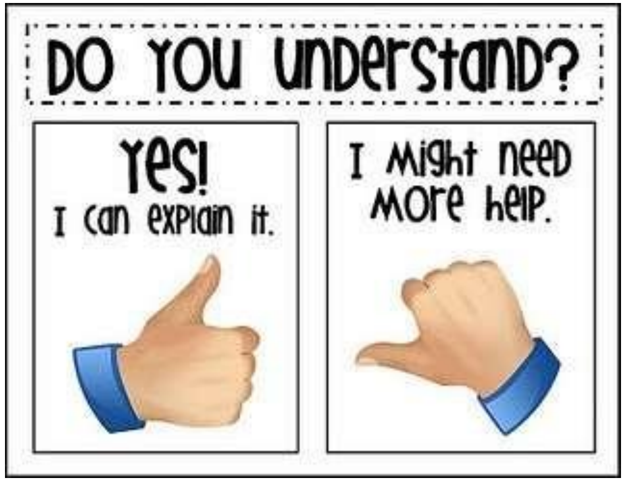
Coimbatore – 641035

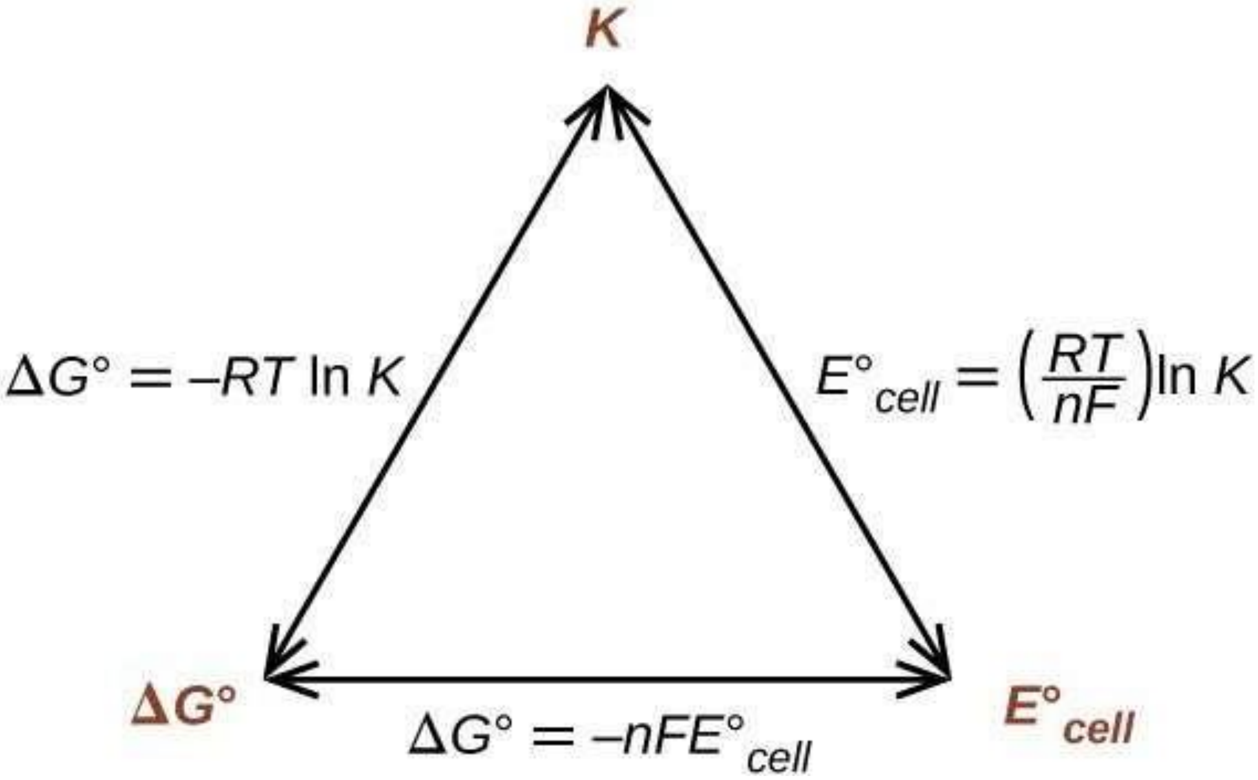
23CHT101-ENGINEERING CHEMISTRY

UNIT 1 - ELECTROCHEMISTRY

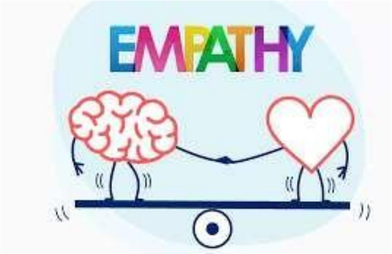
1. 2 Nernst Equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$


DO YOU UNDERSTAND?
YES!
I can explain it.
I Might need more help.


K
$\Delta G° = -RT \ln K$
$E°_{cell} = \left(\frac{RT}{nF}\right) \ln K$
$\Delta G°$
$\Delta G° = -nFE°_{cell}$
$E°_{cell}$

Nernst equation



SAYS

- It's used to calculate electrode potential under non-standard conditions.
- It shows how concentration affects EMF of a cell.
- We use the equation $E = E^{\circ} - 0.959r$ $E = E = \frac{0.0591}{n}$

  at 25°C.

THINKS

- Why does changing concentration change the cell voltage?
- How does this equation link chemistry with thermodynamics?
- Can I use this for any redox reaction or only galyanic cells?
- What's the meaning of 'Q' and 'n' in real-life electrochemical systems

Empathy Map –Nernst Equation

DOES

- Substitutes values into the Nernst equation to calculate cell EMF.
- Plots EMF vs. concentration to visualize potential change.
- Compares experimental EMF with theoretical EMF.
- Learns to derive the equation from Gibbs free energy relation

FEELS

- **Confused** initially by logarithms and thermodynamic symbols
- Curious when realizing how chemistry connects with energy and mathematics
- Satisfied after applying it to real examples like pH calculation and galvanic cells
- Motivated when understanding its practical importance in batteries and sensors

1) Starting point — thermodynamics of a redox cell

For an electrochemical reaction that transfers n moles of electrons, the cell electrical work (electromotive force E) is related to the Gibbs free energy change ΔG:

$$\Delta G = -nFE$$

where

- n = number of moles of electrons transferred,
- F = Faraday constant $\approx 96485 \text{ C mol}^{-1}$,
- E = cell potential (volts).

At standard conditions the same relation holds for standard Gibbs free energy change ΔG° and standard potential E°:

$$\Delta G^\circ = -nFE^\circ$$

Also from thermodynamics the relation between ΔG and the reaction quotient Q is

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

where

- R = gas constant $8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$,
- T = temperature in K,
- Q = reaction quotient (activities, but concentrations are often used in practice).

2) Combine the equations

Substitute $\Delta G = -nFE$ and $\Delta G^{\circ} = -nFE^{\circ}$ into the thermodynamic relation:

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Rearrange to isolate E:

$$-nF(E - E^{\circ}) = RT \ln Q$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

This is the **Nernst equation (natural log form)**.

3) Common practical form (base-10 logarithm)

Chemists usually prefer $\log_{10}$. Use $\ln x = 2.303 \log_{10} x$:

$$E = E^{\circ} - \frac{2.303\, RT}{nF} \log_{10} Q$$

At $T = 298.15\ \mathrm{K}$ (25 °C), the factor $\frac{2.303RT}{F}$ equals approximately $0.05916\ \mathrm{V}$. So:

$$\boxed{E = E^{\circ} - \frac{0.05916}{n} \log_{10} Q \quad (\text{at } 25\ ^{\circ}\mathrm{C})}$$

4) Reaction quotient Q — what to plug in

For a general redox reaction written in net form, write Q using activities (or concentrations if activities aren't given). Example:

For the Zn/Cu cell overall reaction

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

the reaction quotient is

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

(solid activities = 1).

For a single half-cell (reduction) potential versus standard hydrogen electrode you can write the half-cell Nernst equation. Example for $Cu^{2+} + 2e^- \rightarrow Cu(s)$:

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{RT}{2F} \ln\left(\frac{1}{a_{Cu^{2+}}}\right) = E^\circ - \frac{RT}{2F} \ln\left(a_{Cu^{2+}}^{-1}\right) = E^\circ + \frac{RT}{2F} \ln a_{Cu^{2+}}$$

(Conventions differ depending on how you write the half-reaction; be consistent.)

At 25°C, that becomes:

$$E = E^\circ - \frac{0.05916}{2} \log_{10}\left(\frac{1}{[Cu^{2+}]}\right) = E^\circ + \frac{0.05916}{2} \log_{10}[Cu^{2+}]$$

Application of Nernst Equation

www.snsgroups.com

DETERMINATION OF ELECTRODE POTENTIAL

The Nernst equation nelps calculate the electrode potential of half-cells when ion concentrations are not 1 M

CALCULATION OF EMF OF ELECTROCHEMICAL CELLS

It allows the computation of cell EMF under non-standard conditions: Used to predict the direction of spontaneous reactions.

SOLUBILITY PRODUCT (K_{sp}) DETERMIN ATION

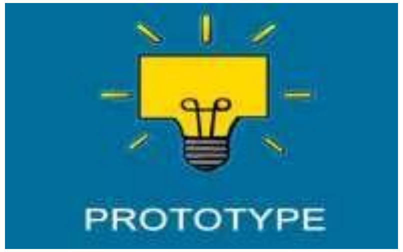
The solubility of sparingly soluble salts cen be calc-ulated from cell potentials using the Nernst equation

DETERMINATION OF EQUILIBRIUM CONSTANT (K)

At equilibrium, cell potential (Ecell) = 0. Substitut-ing into the Nernst equat-ion gives a direct relatoti-nship between E'_{Ceil} and K

UNDERSTANDING CONCENTRATION CELLS

It helps to determine the EMF of concentration cells, where potential arises solely due to concentration differences



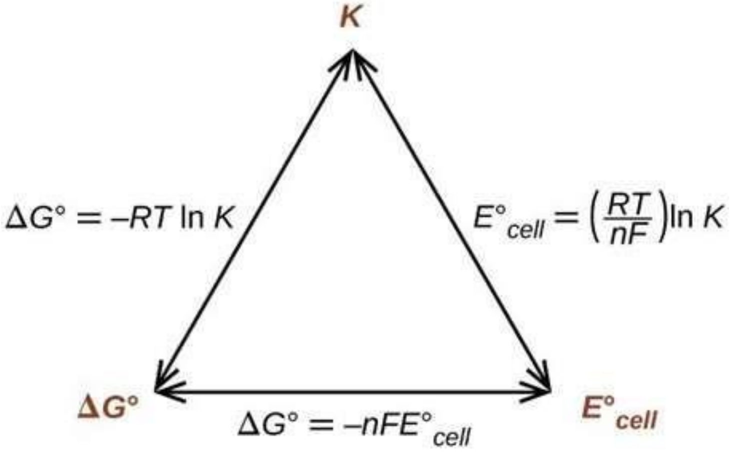
Given standard potentials:

$E^{\circ}_{Cu^{2+}/Cu} = +0.34\ \mathrm{V}$, $E^{\circ}_{Zn^{2+}/Zn} = -0.76\ \mathrm{V}$.

Thus $E^{\circ}_{cell} = 0.34 - (-0.76) = 1.10\ \mathrm{V}$.

If $[Cu^{2+}] = 0.01\ \mathrm{M}$ and $[Zn^{2+}] = 0.1\ \mathrm{M}$, then

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01} = 10$$



Using the Nernst equation at 25 °C with $n = 2$:

$$E = 1.10 - \frac{0.05916}{2}\log_{10}(10) = 1.10 - \frac{0.05916}{2} \times 1 = 1.10 - 0.02958 = 1.0704\ \mathrm{V}$$

25.09.2025

References

https://en.wikipedia.org/wiki/Nernst_equation

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Nernst_Equation