

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT BASED NOTES OF CHAPTER -03)

GANESH KUMAR

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Electrochemistry

Nernst Equation

Nernst proposed an equation to relate the electrode potential of an electrode (or, emf of a cell) with the electrolytic concentration.

He showed that for the electrode reaction:



the electrode potential can be given by:

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

Since the concentration of any solid is taken as unity, the above equation becomes:

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

$$\text{Or, } E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} + \frac{2.303RT}{nF} \log [M^{n+}]$$

$$\text{or, } E_{\text{el.}} = E^0_{\text{el.}} + \frac{2.303RT}{nF} \log [M^{n+}]$$

Where

E^0 is the standard electrode potential;

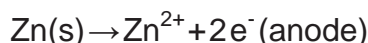
R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

F is Faraday constant (96500 C mol^{-1}),

T is temperature in Kelvin and

$[M^{n+}]$ is the concentration of the species, M^{n+} .

In Daniel cell, the electrode reactions are:



The electrode potentials are given as

For Cathode:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E^0_{(\text{Cu}^{2+}/\text{Cu})} + \frac{RT}{2F} \ln [\text{Cu}^{2+}]$$

$$\text{For anode: } E_{(\text{Zn}^{2+}/\text{Zn})} = E^0_{(\text{Zn}^{2+}/\text{Zn})} + \frac{RT}{2F} \ln [\text{Zn}^{2+}]$$

The cell potential,

$$E_{\text{cell}} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$$
$$= \left\{ E^0_{(\text{Cu}^{2+}/\text{Cu})} + \frac{RT}{2F} \ln [\text{Cu}^{2+}] \right\} - \left\{ E^0_{(\text{Zn}^{2+}/\text{Zn})} + \frac{RT}{2F} \ln [\text{Zn}^{2+}] \right\}$$

$$= [E^0_{(\text{Cu}^{2+}/\text{Cu})} - E^0_{(\text{Zn}^{2+}/\text{Zn})}] + \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\text{Or, } E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

On changing the base of logarithm, we get

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{2.303RT}{2F} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

On substituting the values of R (8.314 JK⁻¹ mol⁻¹), F(96500 C mol⁻¹) at 298K, the above equation becomes,

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

For a general electrochemical reaction of the type:



Nernst equation can be written as:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{A}]^a [\text{B}]^b}{[\text{C}]^c [\text{D}]^d}$$

Equilibrium Constant from Nernst Equation

For a Daniel cell, the emf of the cell at 298K is given by:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

When the cell reaction attains equilibrium, $E_{\text{cell}} = 0$

$$\text{So, } 0 = E_{\text{cell}}^0 + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\begin{aligned} \text{Or, } E_{\text{cell}}^0 &= -\frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \\ &= \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \end{aligned}$$

But at equilibrium, $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_c$

So the above equation becomes,

$$E_{\text{cell}}^0 = \frac{0.0591}{2} \log K_c$$

In General, $E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log K_c$

$$\text{or, } E_{\text{cell}}^0 = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K}$$

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. Also the reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, if the emf of the cell is E and nF is the amount of charge passed,

then the Gibbs energy of the reaction, $\Delta G = -nFE_{\text{cell}}$

If the concentration of all the reacting species is unity, then $E_{\text{cell}} = E_{\text{cell}}^0$.

So, $\Delta G^0 = -nFE_{\text{cell}}^0$

Thus, from the measurement of E_{cell}^0 , we can calculate the standard Gibbs energy of the reaction.
