ELECTRO-CHEMICAL AND GIBB'S ENERGY

Electrochemistry

This field of study within chemistry explores the correlation between chemical energy and electrical energy, as well as the conversions between the two.

Redox Reactions

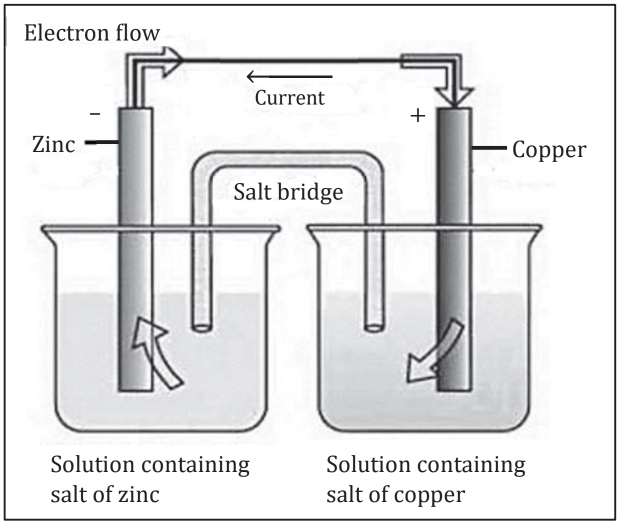
Oxidation is the phenomenon characterized by the loss of electrons, while reduction is a process involving the gain of electrons. When a reaction encompasses both these processes simultaneously, it is referred to as a redox reaction.

Electrochemical Cells

These are apparatuses that transform the chemical energy from certain redox reactions into electrical energy. They are alternatively known as Galvanic cells or Voltaic cells, with the Daniel cell serving as an example. The construction involves immersing a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are externally connected by a metallic wire through a voltmeter and a switch, and internally connected by a salt bridge. The salt bridge is a U-tube containing an inert electrolyte, such as $NaNO_3$ or KNO_3, within a gel-like substance.

The functions of a salt bridge are

1. To complete the electrical circuit
2. To maintain the electrical neutrality in the two half cells.
   - ➢ $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction)
   - ➢ $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)



These reactions take place in distinct segments of the Daniel cell. The reduction half-reaction transpires on the copper electrode, whereas the oxidation half-reaction transpires on the zinc electrode. These segments of the cell are also referred to as half-cells or redox couples. Specifically, the copper electrode may be designated as the reduction half-cell, and the zinc electrode as the oxidation half-cell.

Electrochemical Cells Nernst Equation and Gibbs Energy

Electrode Potential

The inclination of a metal to either loss or gain an electron when in contact with its own solution is termed electrode potential.

Standard electrode potential (E^0)

The electrode potential is determined under standard conditions, i.e., at 298K, 1 atm pressure, and a concentration of 1 molar.

Standard hydrogen electrode (SHE)

The reference electrode employed for measuring individual electrode potential is presumed to have a potential of zero. It comprises a platinum wire immersed in a 1 molar concentration of HCl, with hydrogen gas at 1 atm passed through the solution.

The electrode can be represented as: $Pt, H_2 / H^+(1M)$.

Nernst Equation for A Cell Reaction

Let us consider a general equation

$$aA + bB \rightarrow cC + dD$$

$$E = E^0_{cell} - \frac{2.303\ RT}{nF} \times \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Where E^0 is the standard electrode potential,

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

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

T is the temperature in Kelvin.

Nernst equation can be written as

Putting the above values Nernst equations can be written as

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

Equilibrium Constant from Nernst Equation

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

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

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

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

or, $$E^0_{cell} = \frac{-0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

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

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

So the above equation becomes,

$$E^0_{cell} = \frac{0.0591}{2} \log\ Kc$$

In General, $$E^0_{cell} = \frac{2.303RT}{nF} \log\ Kc$$

or, $$E^0_{cell} = \frac{0.0591}{n} \log\ Kc \text{ at 298 K}$$

Electrochemical Cells Nernst Equation and Gibbs Energy

Electrochemical Cell and Gibbs Energy of the Reaction

The electrical work accomplished in a single second is equivalent to the electrical potential multiplied by the total charge transferred. The reversible work performed by a galvanic cell is equal to the reduction in its Gibbs energy. Therefore, if the electromotive force (emf) of the cell is denoted as E, the quantity of charge transferred is represented by nF, and ΔG signifies the Gibbs energy change of the reaction, then

$$\Delta G = - \ nFE_{cell}$$

If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$ and we have

$$\Delta G^0 = - nFE^0{}_{cell}$$

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