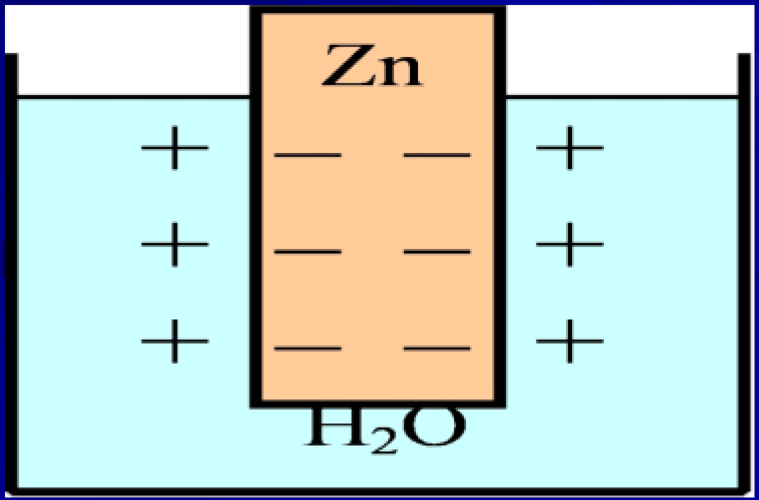
Electrode Potentials

Medical Chemistry

Mechanism of formation of electrode potential

A metal plate is immersed in water. It loses cations. The plate obtains a negative charge. The negative charge layer and positive ions surrounding it make the double electrical layer (DEL).



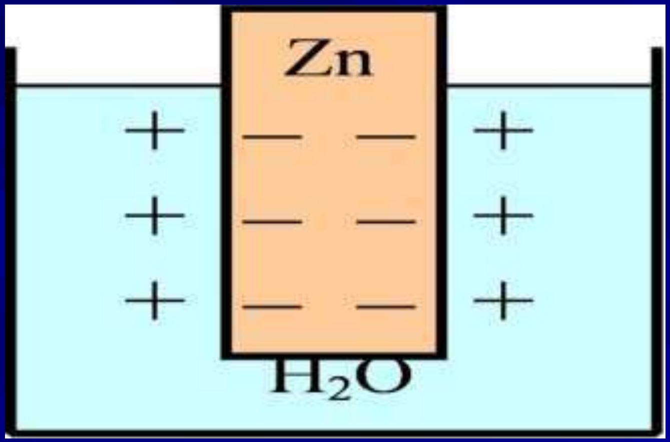
Mechanism of formation of electrode potential

A metal plate can be immersed in a solution of a salt of the metal. Depending on molarity of the metal ions, they can be adsorbed on the plate or lost into the solution. The electrode potential changes accordingly.

The identity of the metal and the molarity of its ions determine electrode potential.

Double electrical layer

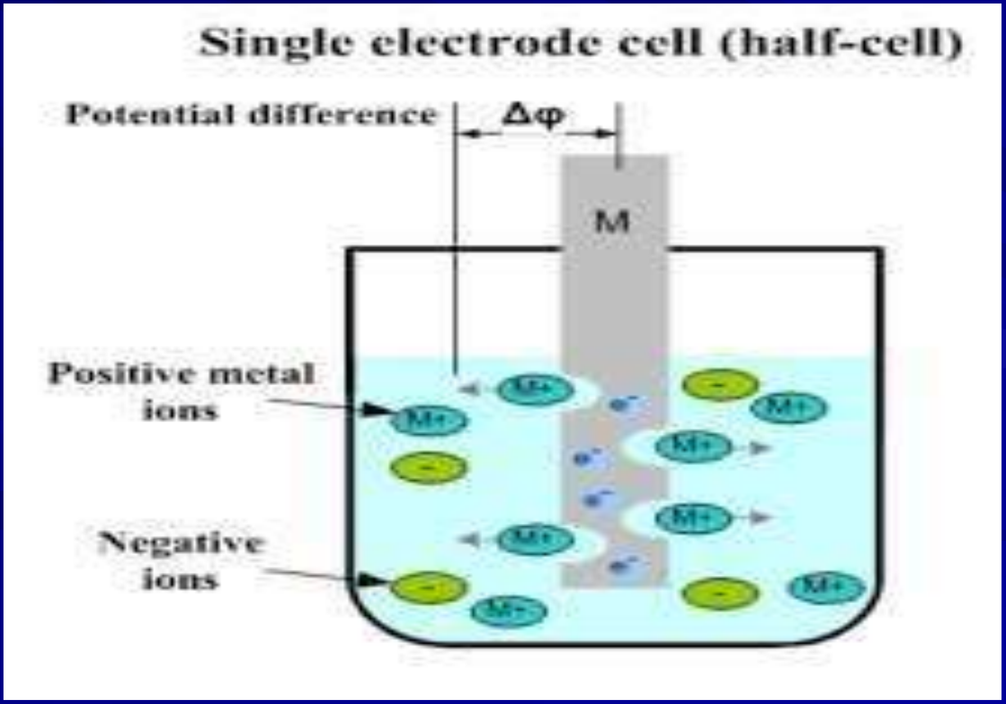
The negative charge layer and positive ions surrounding it make the double electrical layer (DEL).



A double electrical layer (DEL) is two parallel layers of charge on a solid surface in a liquid phase.

Electrode potential

Electrode potential is a difference of potentials at an electrode-electrolyte interface at equilibrium.



Nernst equation

The Nernst equation describes electrode potential:

$$E = E^0 + \frac{RT}{nF} ln[M^{n+}]$$

- E^0 is the standard electrode potential;
- R is the universal gas constant;
- n is the number of transferred electrons;
- F is the Faraday constant;
- $\alpha(Me^{n+})$ is the activity of the metal ion in solution, mol/L.

Nernst equation

Note that for diluted solutions activity of ions is equal to concentration of the ions.

From the Nernst equation, electrode potential depends on identity of the metal (E^0, n), temperature and concentration of the salt of the metal.

Simplified Nernst equation

At 25 C (298 K), the Nernst equation is as follows:

$$E = E^0 + \frac{0.059}{n} lg[M^{n+}]$$

Standard electrode potential

Standard electrode potential E^0 is the potential of an electrode in a solution with activity of ions 1 mol/L at the pressure of 1 atm and at 25 °C.

E^0 depends on the identity of the metal.

Standard electrode potentials are used to compare oxidative and reductive strengths.

More negative standard electrode potential = stronger reducing agent

Measurement of electrode potentials

Necessary equipment:

- An ionic meter device
- Two electrodes:

  indicator electrode

  reference electrode.

Measurement of electrode potentials

It measures electromotive force (EMF) between the electrodes.

EMF is the difference between the potentials of two points in a galvanic cell.

Indicator electrodes

Indicator electrode interacts with a substance in solution resulting in a change of its potential depending on its concentration in the solution

Examples:

Glass electrode – to measure pH,

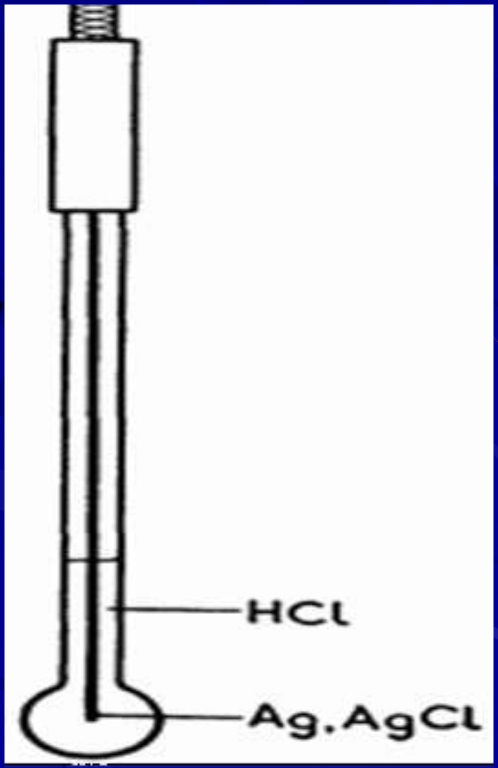
Na-selective electrode – to measure concentration of sodium ions

Indicator electrodes

Glass electrode is a membrane electrode.

The glass membrane exchanges ions of sodium for ions of hydrogen.

The potential of the electrode changes depending on molarity of hydrogen ions (pH).



Reference electrode

Reference electrode does not interact with substances in solution, and its potential is constant.

Examples:

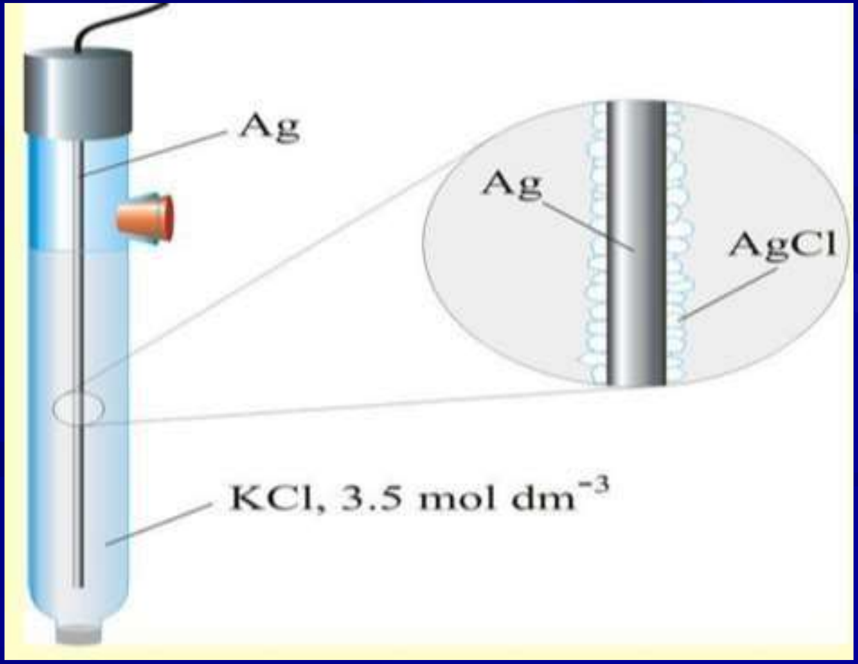
Silver–silver chloride electrode,

calomel electrode

standard hydrogen electrode

Reference electrode

Silver–silver chloride electrode consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration.



Measurement vs calculation of electrode potentials

Electrode potentials are measured in order to calculate concentrations of ions in solutions with the Nernst equation.

Standard hydrogen electrode (SHE)

Importance:

The standard hydrogen electrode has the standard electrode potential of 0 V and is used to obtain values of all other standard electrode potentials.

Standard hydrogen electrode (SHE)

Process:

$$2\ H^+ + 2\ e^- \leftrightarrow H_2$$

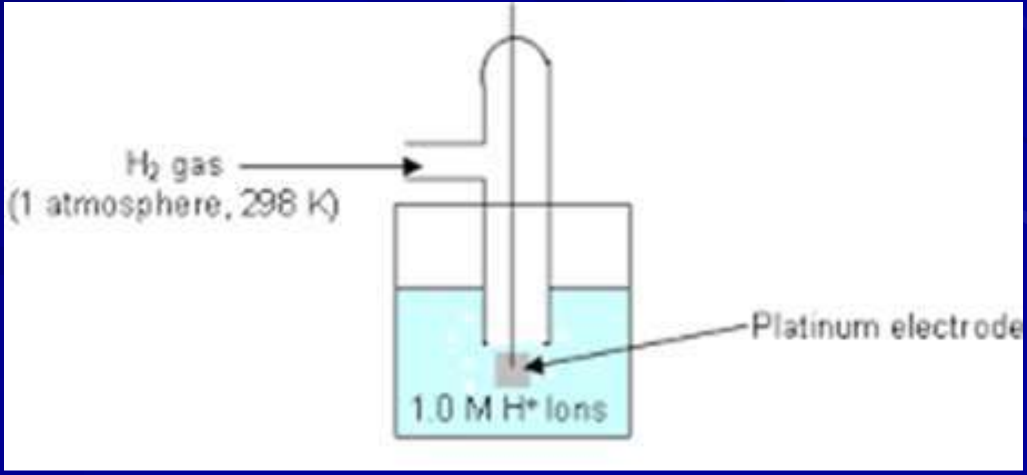
Nernst equation:

$$E_{hydrogen} = -0.059\ pH$$

As a measurement electrode, SHE is used to measure pH.

Standard hydrogen electrode (SHE)

Structure: It is a platinized platinum electrode immersed in an water solution where activity of the H+ ions is 1 mol/L. The concentration of H+ ions in the solution is in equilibrium with H2 gas bubbled through the solution at a pressure of 1 atm at the Pt-solution interface



Redox reactions

Redox reactions are all chemical reactions in which oxidation states of atoms are changed due to transfer of electrons between reacting species.

Oxidation is loss of electrons and increase in oxidation state of a chemical species.

Reduction is gain of electrons and decrease in oxidation state of a chemical species

Redox systems

Redox system contains oxidized and reduced forms of the same substance.

Examples:

Fe^{3+}/Fe^{2+}

Cu^{2+}/Cu^{+}

$NADH/NAD^{+}$

pyruvate/lactate

Nernst-Peters equation

It is used to calculate the potential of a redox system:

$$E_{ox|red} = E^0_{ox|red} + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}}$$

The potential of a redox system depends on its identity, temperature and the ratio of oxidized and reduced forms.

At 298 K: $$E_{ox|red} = E^0_{ox|red} + \frac{0.059}{n}\lg\frac{a_{ox}}{a_{red}}$$

Standard redox potential

A standard redox potential is the potential of an inert electrode in a solution with activities of reduced and oxidized species equal to 1 mol/L at the pressure of 1 atm and at 25 °C.

In addition, biochemical E^0 values are measured at pH = 7.

Standard redox potential

E^0 values are used to compare strength of oxidizing or reducing agents.

The more positive E^0 value, the stronger oxidizing agent. The more negative E^0 value, the stronger reducing agent.

Examples:

E^0 (Fe^{2+}/Fe^{3+}) = +0.77,

and E^0 (Co^{2+}/Co^{3+}) = +1.84.

The stronger oxidizing agent is cobalt.

Measurement of redox potentials

Indicator electrodes are inert electrodes:

platinum electrode

gold electrode

They transfer electrons and do not exchange ions with the solution.

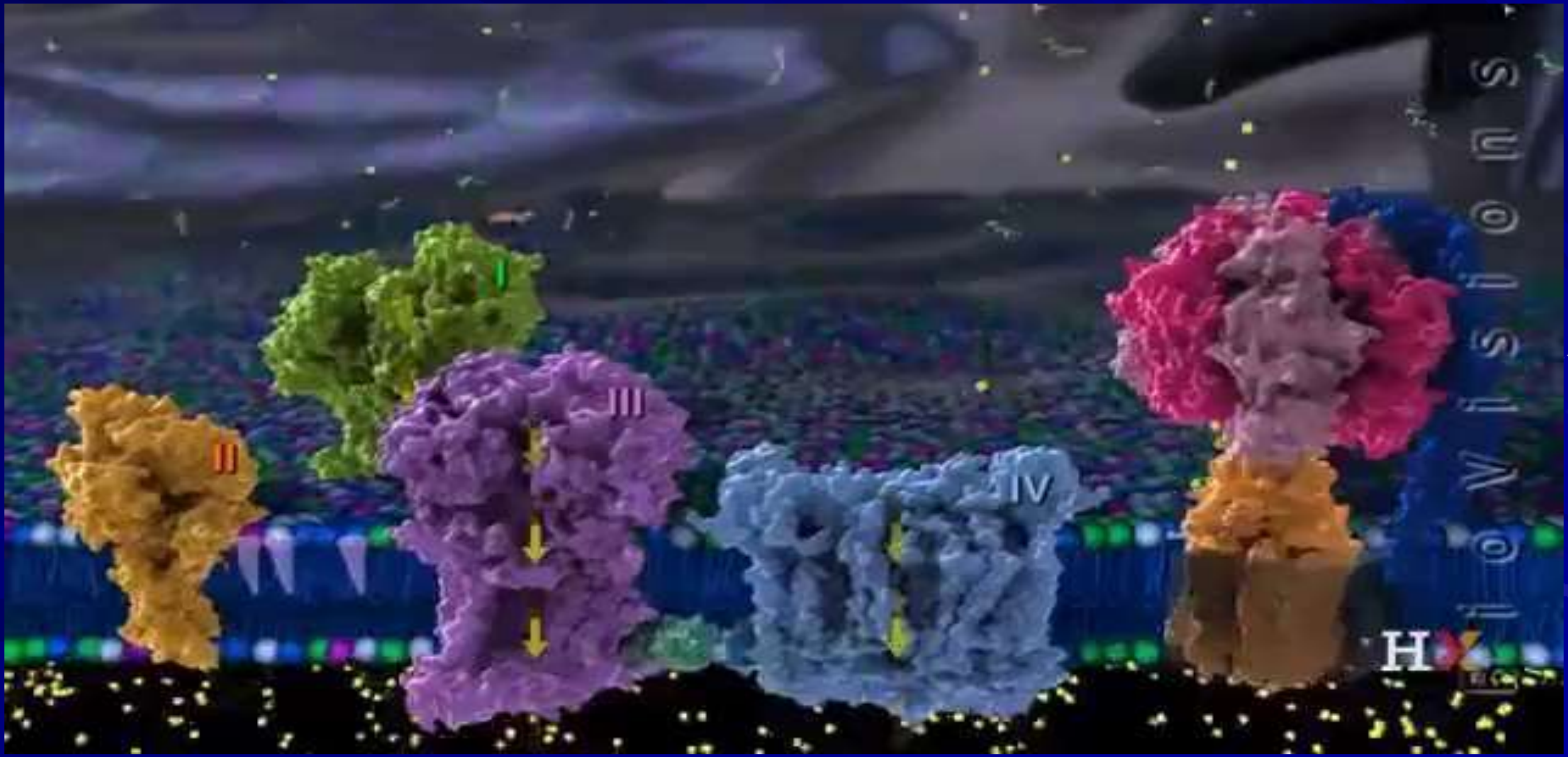
Redox reactions in the organism

Biological oxidation is the main source of energy in the organism.

It proceeds in multiple steps, with a small amount of energy released at each step.
It allows for efficient use of the energy.

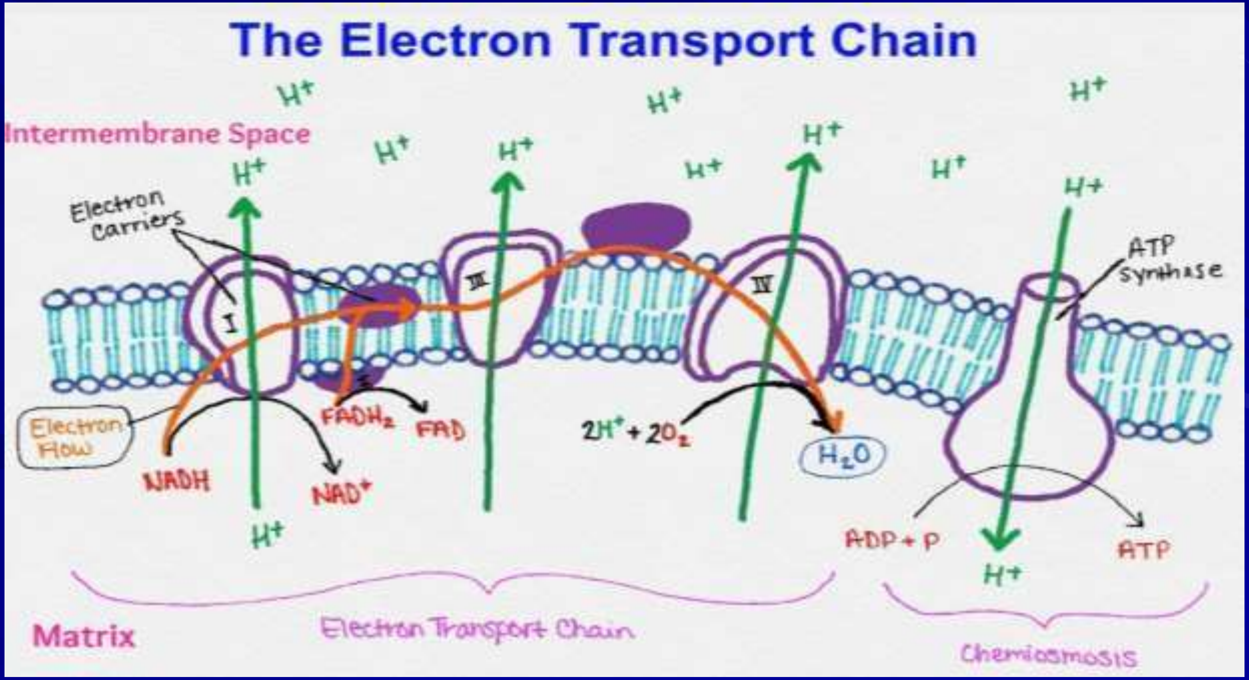
Electron transport chain (ETC)

ETC is the hub of metabolic processes.



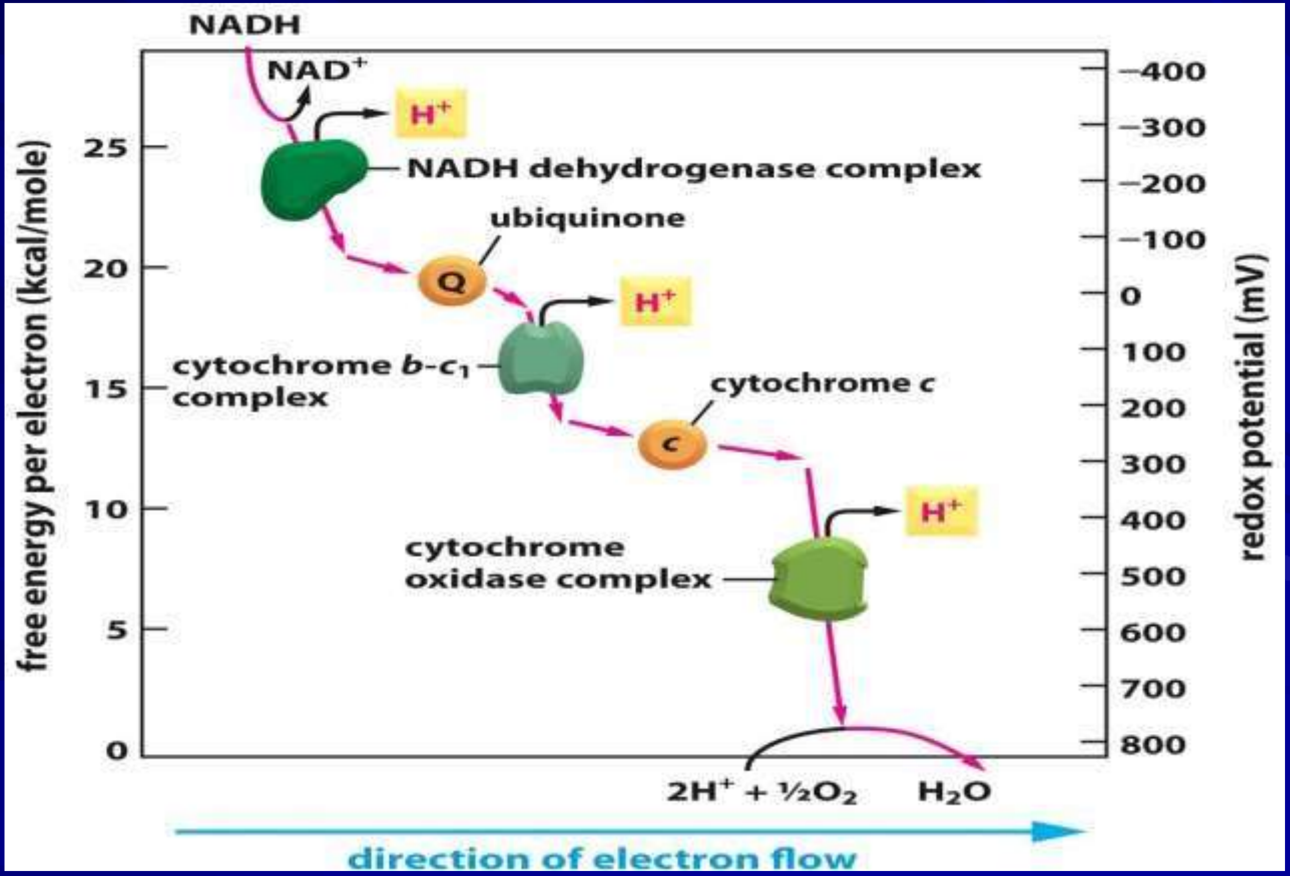
Electron transport chain

ETC is called tissue respiration because it consumes oxygen. It is found in mitochondria. Components of the ETC are placed on the inner mitochondrial membrane along values of their redox potentials.



Electron transport chain

Transfer of electrons proceeds from most negative to most positive component.



Electron transport chain

e.g., electrons move from cytochrome oxidase Fe^{3+}/Fe^{2+} (E^0 = 0.29 V) to O_2/H_2O (E^0 = 0.82 V), and O_2 is reduced to H_2O:

$$2\bar{e} + \frac{1}{2}O_2 + 2H^+ \rightleftarrows H_2O$$

Oxygen is the final acceptor of protons and electrons in the ETC.

Membrane potential

Membrane potential is the difference of potentials between the interior and the exterior of a biological cell.

Typically, values of membrane potential range from –40 mV to –80 mV.

It is maintained by Na+/K+ ATPase.

It transports three sodium ions out of the cell and two potassium ions in.