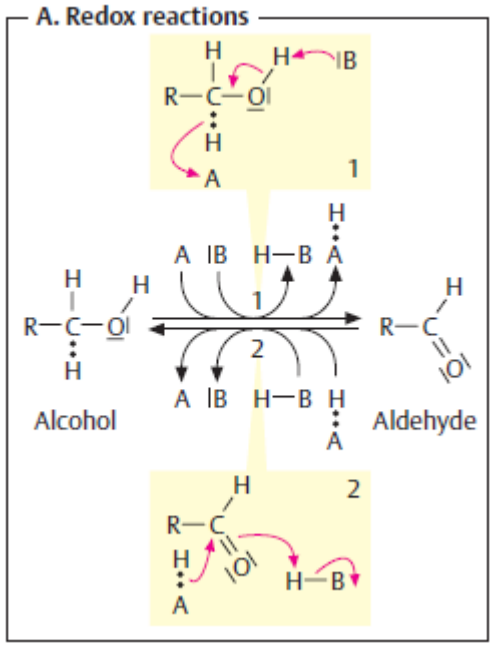
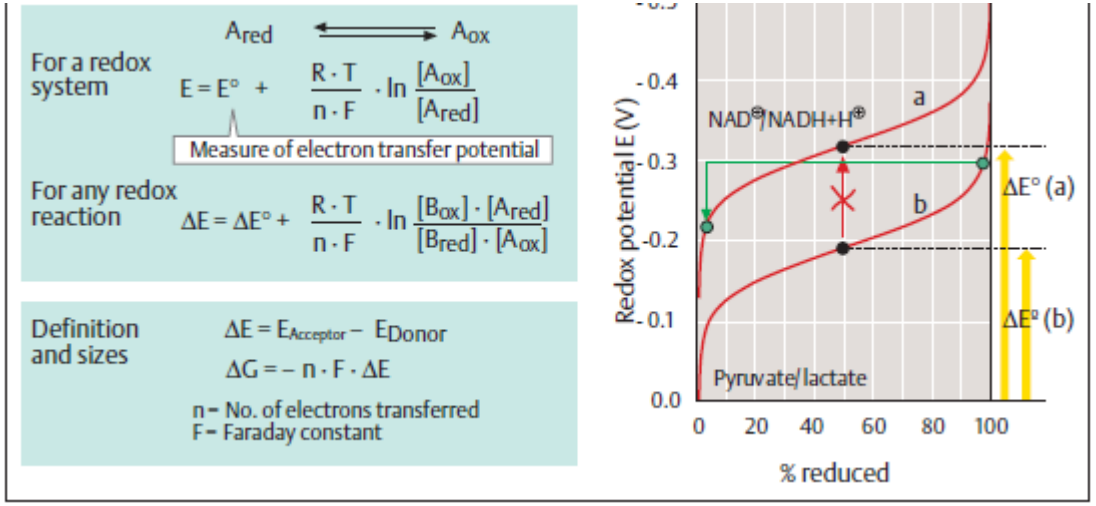
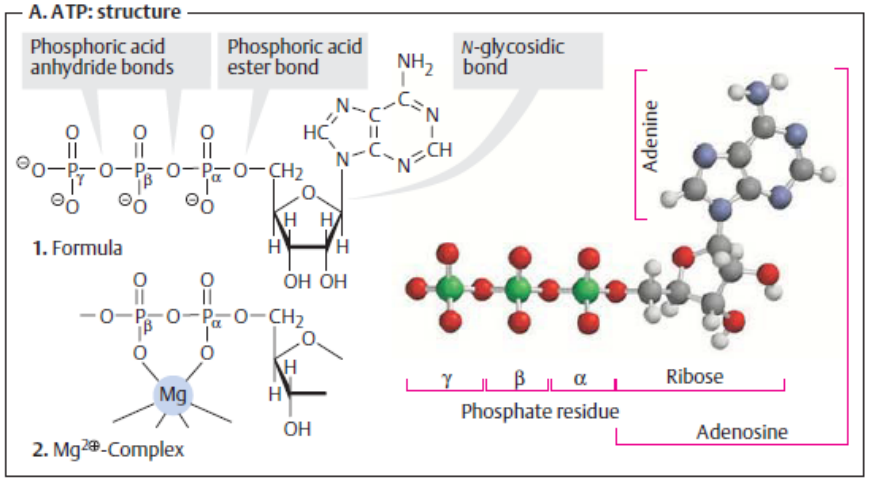
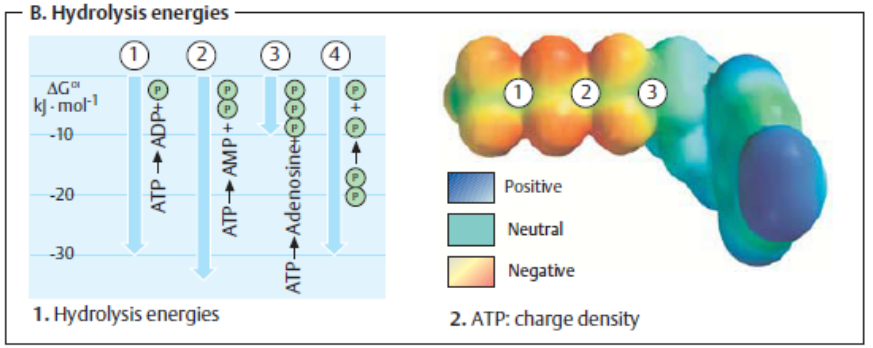
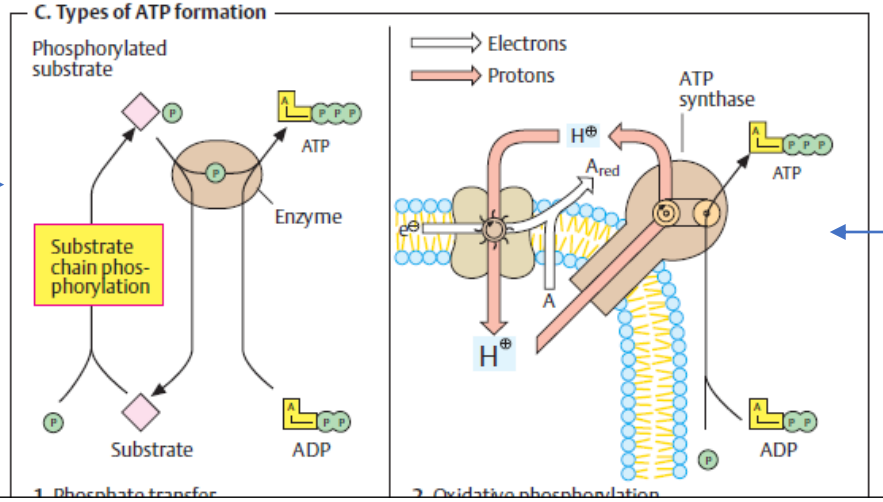


The course of electron transfer reactions (redox reactions also follows the law of mass action. For a single redox system the Nernst equation applies. The electron transfer potential of a redox system (i. e., its tendency to give off or take up electrons) is given by its redox potential E (in standard conditions, E0 or E0').
The lower the redox potential of a system is, the higher the chemical potential of the transferred electrons. To describe reactions between two redox systems, ΔE—the difference between the two systems' redox potentials—is usually used instead of ΔG. ΔG and ΔE have a simple relationship, but opposite signs. A redox reaction proceeds spontaneously when ΔE > 0, i.e. ΔG < 0. Redox potential E is dependent on the composition (the proportion of the reduced form as a %) in two biochemically important redox systems (pyruvate/lactate and NAD+/NADH+H+).
In the standard state (both systems reduced to 50%), electron transfer from lactate to NAD+ is not possible, because ΔE is negative (ΔE = –0.13 V). By contrast, transfer can proceed successfully if the pyruvate/lactate system is reduced to 98% and NAD+/NADH is 98% oxidized (ΔE = +0.08 V).









Substrate-level phosphorylation

Oxidative phosphorylation

Phosphorylation Potential (Δg_p)
The change in free energy within the cell after hydrolysis of ATP. The **phosphorylation potential**, $\Delta G\ P = \Delta G\ 0\ ' + 1.36 \log ([ATP]\ [ADP][P\ i\ ])$, where $\Delta G_O'$ is the standard free energy of hydrolysis of ATP at a given pH, and [ATP], [ADP] and [P_i] refer to concentrations in the suspending medium, has been determined in rat-liver mitochondria under various conditions.

The **redox potential** is used to describe a system's overall reducing or oxidizing capacity. The redox potential is measured in millivolts (mV) relative to a standard hydrogen electrode and is commonly measured using a platinum electrode with a saturated calomel electrode as reference.

Many enzymatic reactions are oxidation–reduction reactions, in which one compound is oxidized and another compound is reduced. The ability of an organism to carry out oxidation–reduction reactions depends on the oxidation–reduction state of the environment, or its reduction potential (E_h).
Strictly aerobic microorganisms are generally active at positive E_h values, whereas strict anaerobes are generally active at negative E_h values.
Redox affects the solubility of nutrients, especially metal ions.
There are organisms that can adjust their metabolism to their environment, such as facultative anaerobes. Facultative anaerobes can be active at positive E_h values, and at negative E_h values in the presence of oxygen-bearing inorganic compounds, such as nitrates and sulfates.

A **standard redox potential**, symbol E^o, is the electric **potential** of an **electrochemical** half-cell relative to a **standard electrochemical** half-cell under **standard** conditions. **Standard redox potential** is also known as the **standard reduction potential**. In biology, the standard reduction potential is the tendency for a chemical species to be reduced, and is measured in volts at standard conditions. The more positive the potential is the more likely it will be reduced.

In biology, redox or oxidoreduction potential is defined as the sum of all the oxidizing (dissolved oxygen, free radicals, hydrogen peroxide, some oxidized metal ions…) and reducing (some vitamins, some reduced metal ions, thiol-containing molecules, hydrogen…) couples found in the medium. Everyday redox reactions include photosynthesis, respiration, combustion and corrosion.

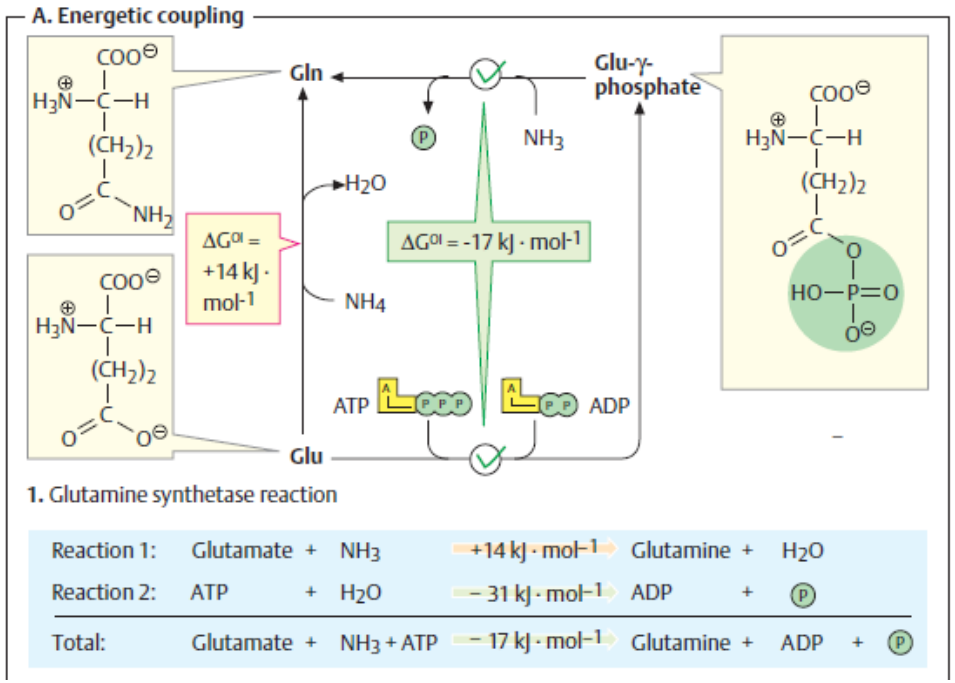
Energetic coupling

The cell stores chemical energy in the form of “energy-rich” metabolites. The most important metabolite of this type is adenosine triphosphate (ATP),which drives a large number of energy-dependent reactions via energetic coupling.

A. Energetic coupling

The change in free enthalpy ΔG0 during hydrolysis has been arbitrarily selected as a measure of the group transfer potential of “energy-rich” compounds. However, this does not mean that ATP is in fact hydrolyzed in energetically coupled reactions. If ATP hydrolysis and an endergonic process were simply allowed to run alongside each other, the hydrolysis would only produce heat, without influencing the endergonic process. For coupling, the two reactions have to be linked in such a way that a common intermediate arises. For example: glutamine synthetase reaction. Direct transfer of NH_3 to glutamate is endergonic ($\Delta G0' = +14$ kJ mol–1), and can therefore not take place. In the cell, the reaction is divided into two exergonic steps. First, the γ-phophate residue is transferred from ATP to glutamate. This gives rise to an “energy-rich” mixed acid anhydride. In the second step, the phosphate residue from the intermediate is substituted by NH_3, and glutamine and free phosphate are produced.

The energy balance of the reaction as a whole ($\Delta G0' = -17$ kJ mol–1) is the sum of the changes in free enthalpy of direct glutamine synthesis ($\Delta G0' = 14$ kJ mol–1) plus ATP hydrolysis ($\Delta G0' = -31$ kJ mol–1), although ATP has not been hydrolyzed at all.



The factor R T/F n has a value of 0.026 V for monovalent ions at 25 °C. Thus, for K+, gives an equilibrium potential of ca. –0.09 V—i. e., a value more or less the same as that of the resting potential. By contrast, for Na+ ions, ΔψG is much higher than the resting potential, at +0.07 V. Na+ ions therefore immediately flow into the cell when Na+ channels open. The disequilibrium between Na+ and K+ ions is constantly maintained by the enzyme Na+/ K+-ATPase, which consumes ATP.

Energy conservation at membranes

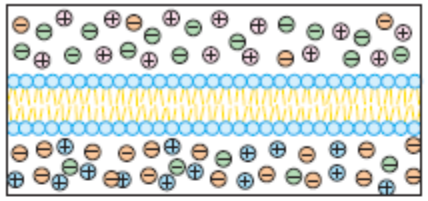
Metabolic energy can be stored not only in the form of "energy-rich" bonds, but also by separating electric charges from each other using an insulating layer to prevent them from redistributing. In the field of technology, this type of system would be called a condenser. Using the same principle, energy is also stored ("conserved") at cell membranes. The membrane functions as an insulator; electrically charged atoms and molecules (ions) function as charges.

A. Electrochemical gradient

Although artificial lipid membranes are almost impermeable to ions, biological membranes contain ion channels that selectively allow individual ion types to pass through. Whether an ion can cross this type of membrane, and if so in which direction, depends on the electrochemical gradient— i. e., on the concentrations of the ion on each side of the membrane (the concentration gradient) and on the difference in the electrical potential between the interior and exterior, the membrane potential. The membrane potential of resting cells (resting potential) is –0.05 to –0.09 V—i. e., there is an excess negative charge on the inner side of the plasma membrane. The main contributors to the resting potential are the two cations Na+ and K+, as well as Cl– and organic anions (1). Data on the concentrations of these ions outside and inside animal cells, and permeability coefficients, are shown in the table (2).

The behavior of an ion type is described quantitatively by the Nernst equation (3). ΔψG is the membrane potential (in volts, V) at which there is no net transport of the ion concerned across the membrane (equilibrium potential).

A. Electrochemical gradient



⊕ Na ⊕ K ⊖ Cl ⊖ Organic anions

1. Cause

Ion	Concentrations		Permeability coefficient
	Cyto-plasm (mM)	Extracelluar space (mM)	($cm \cdot s^{-1} \cdot 10^9$)
$K^{\oplus}$	100	5	500
$Na^{\oplus}$	15	150	5
$Ca^{2\oplus}$	0.0002	2	
$Cl^{\ominus}$	13	150	10
Organic anions	138	34	0

2. Concentrations

$$\Delta\Psi_G = \frac{R \cdot T}{F \cdot n} \cdot \ln \frac{C_{outside}}{C_{inside}}$$

R = gas constant
T = temperature (K)
n = Ion charge
F = Faraday constant

3. Nernst equation

(1) In electrochemistry, the *Nernst equation* is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation. It was named after Walther Nernst, a German physical chemist who

A quantitative relationship between cell potential and concentration of the ions
$Ox + z\ e^- \rightarrow Red$
standard thermodynamics says that the actual free energy change ΔG is related to the free energy change under standard state ΔG^o
by the relationship:

where Q_r is the reaction quotient. The cell potential E associated with the electrochemical reaction is defined as the decrease in Gibbs free energy per coulomb of charge transferred, which leads to the relationship .
The constant F (the Faraday constant) is a unit conversion factor $F = N_A q$, where N_A is Avogadro's number and q is the fundamental electron charge. This immediately leads to the Nernst equation, which for an electrochemical half-cell is
.
For a complete electrochemical reaction (full cell), the equation can be written as

where
E_{red} is the half-cell reduction potential at the temperature of interest,
E^o
$_{red}$ is the *standard* half-cell reduction potential,
E_{cell} is the cell potential (electromotive force) at the temperature of interest,
E^o
$_{cell}$ is the standard cell potential,
R is the universal gas constant: $R = 8.31446261815324\ J\ K^{-1}\ mol^{-1}$,
T is the temperature in kelvins,
z is the number of electrons transferred in the cell reaction or half-reaction,
F is the Faraday constant, the number of coulombs per mole of electrons: $F = 96485.3321233100184\ C\ mol^{-1}$,
Q_r is the reaction quotient of the cell reaction, and
a is the chemical activity for the relevant species, where a_{Red} is the activity of the reduced form and a_{Ox} is the activity of the oxidized form.

The Nernst equation has a physiological application when used to calculate the potential of an ion of charge *z* across a membrane. This potential is determined using the concentration of the ion both inside and outside the cell:

$$E = \frac{RT}{zF} \ln \frac{[\text{ion outside cell}]}{[\text{ion inside cell}]} = 2.3026 \frac{RT}{zF} \log_{10} \frac{[\text{ion outside cell}]}{[\text{ion inside cell}]}.$$

When the membrane is in thermodynamic equilibrium (i.e., no net flux of ions), the membrane potential must be equal to the Nernst potential. However, in physiology, due to active ion pumps, the inside and outside of a cell are not in equilibrium. In this case, the resting potential can be determined from the Goldman equation, which is a solution of G-H-K influx equation under the constraints that total current density driven by electrochemical force is zero:

$$E_{\mathrm{m}} = \frac{RT}{F} \ln \left(\frac{\sum_i^N P_{\mathrm{M}_i^+} \left[\mathrm{M}_i^+\right]_{\mathrm{out}} + \sum_j^M P_{\mathrm{A}_j^-} \left[\mathrm{A}_j^-\right]_{\mathrm{in}}}{\sum_i^N P_{\mathrm{M}_i^+} \left[\mathrm{M}_i^+\right]_{\mathrm{in}} + \sum_j^M P_{\mathrm{A}_j^-} \left[\mathrm{A}_j^-\right]_{\mathrm{out}}} \right),$$

where

E_m is the membrane potential (in volts, equivalent to joules per coulomb),
P_{ion} is the permeability for that ion (in meters per second),
$[ion]_{out}$ is the extracellular concentration of that ion (in moles per cubic meter, to match the other SI units, though the units strictly don't matter, as the ion concentration terms become a dimensionless ratio),
$[ion]_{in}$ is the intracellular concentration of that ion (in moles per cubic meter),
R is the ideal gas constant (joules per kelvin per mole),
T is the temperature in kelvins,
F is Faraday's constant (coulombs per mole).

The potential across the cell membrane that exactly opposes net diffusion of a particular ion through the membrane is called the Nernst potential for that ion. As seen above, the magnitude of the Nernst potential is determined by the ratio of the concentrations of that specific ion on the two sides of the membrane. The greater this ratio the greater the tendency for the ion to diffuse in one direction, and therefore the greater the Nernst potential required to prevent the diffusion. A similar expression exists that includes *r* (the absolute value of the transport ratio). This takes transporters with unequal exchanges into account. See: sodium-potassium pump where the transport ratio would be 2/3, so r equals 1.5 in the formula below. The reason why we insert a factor r = 1.5 here is that current density *by electrochemical force* $J_{e.c.}(Na^+)+J^{e.c.}(K^+)$ is no longer zero, but rather $J_{e.c.}(Na^+)+1.5J_{e.c.}(K^+)=0$ (as for both ions flux by electrochemical force is compensated by that by the pump, i.e. $J_{e.c.}=-J_{pump}$), altering the constraints for applying GHK equation. The other variables are the same as above. The following example includes two ions: potassium (K^+) and sodium (Na^+). Chloride is assumed to be in equilibrium

$$E_m = \frac{RT}{F} \ln \left(\frac{rP_{\mathrm{K}^+} \left[\mathrm{K}^+\right]_{\mathrm{out}} + P_{\mathrm{Na}^+} \left[\mathrm{Na}^+\right]_{\mathrm{out}}}{rP_{\mathrm{K}^+} \left[\mathrm{K}^+\right]_{\mathrm{in}} + P_{\mathrm{Na}^+} \left[\mathrm{Na}^+\right]_{\mathrm{in}}} \right).$$

When chloride (Cl^-) is taken into account,

$$E_m = \frac{RT}{F} \ln \left(\frac{rP_{\mathrm{K}^+} \left[\mathrm{K}^+\right]_{\mathrm{out}} + P_{\mathrm{Na}^+} \left[\mathrm{Na}^+\right]_{\mathrm{out}} + P_{\mathrm{Cl}^-} \left[\mathrm{Cl}^-\right]_{\mathrm{in}}}{rP_{\mathrm{K}^+} \left[\mathrm{K}^+\right]_{\mathrm{in}} + P_{\mathrm{Na}^+} \left[\mathrm{Na}^+\right]_{\mathrm{in}} + P_{\mathrm{Cl}^-} \left[\mathrm{Cl}^-\right]_{\mathrm{out}}} \right).$$