

Chemical Thermodynamics Review

- ❖ Most biological reactions are oxidation reduction reactions. A redox reaction is a coupled reaction that involves the transfer of electrons from one molecule to another.
 - Oxidation - the molecule or atom loses electrons.
 - Usually we can tell a compound is oxidized because it gains oxygen, loses hydrogen or gains a more positive charge.
 - The compound that is oxidized can be referred to as an electron donor or a reducing agent.
 - Reduction - the molecule or atom gains electrons.
 - Usually we can tell a compound is reduced because it loses oxygen, gains hydrogen or gains a more negative charge.
 - The compound that is reduced can be referred to as an electron acceptor or an oxidizing agent.
 - The two molecules involved are called a redox pair.
- ❖ Balancing redox reactions by the half reaction method (acidic or neutral conditions):
 - Step 1. Write the reaction as two half reactions, one oxidation and one reduction.
 - Step 2. Balance all compounds that are not O or H.
 - Step 3. Balance O by adding H₂O to the side deficient in O.
 - Step 4. Balance H by adding H⁺ to the side deficient in H.
 - Step 5. Balance charge by adding e⁻ to the more positive charge.
 - Step 6. Multiply each half reaction by some factor to have the same number of electrons transferred in each half reaction.
 - Step 7. Add the two half reactions together and clean up.
 - Step 8. Check that all elements and charge are in balance.
- ❖ **Free energy of a reaction** - when a chemical reaction takes place, a change in energy occurs. The amount of energy released can be expressed as:
 - H - enthalpy - total amount of energy released
 - G - Gibbs free energy - energy available to do useful work $\Delta G = \Delta H - T\Delta S$
 - If ΔG is negative, energy is released (the reaction is spontaneous) if ΔG is positive, energy is needed to drive the reaction (the reverse reaction is spontaneous).

❖ The change in free energy during a reaction can be computed from:

$$\Delta G = \Delta G^{\circ} + RT \ln \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right] = \Delta G^{\circ} + RT \ln Q$$

where ΔG is the change in free energy under the given conditions (kJ), ΔG° is the standard change in free energy at pH 7 (kJ), R is the ideal gas constant, T is the absolute temperature.

⇒ **Free energy of formation** (G_f°) - the energy released or required to form one mole of molecules from its elements. These values are tabulated (see Appendix A in your textbook). By convention the G_f° of the elements (O_2 , N_2 , C) is zero. One can calculate the free energy for a reaction using a balanced chemical equation and the tabulated G_f° values as:

$$\Delta G^{\circ} = \sum G_f^{\circ} \text{ products} - \sum G_f^{\circ} \text{ reactants}$$

The difference in electrical potential between two redox pairs is expressed as the ΔE_o , and is directly proportional to ΔG° :

$$\Delta G^{\circ} = -nF\Delta E_o$$

where n is the number of electrons transferred and F is Faraday constant (96,630 J/V).

⇒ **Free energy and equilibrium** - at equilibrium the forward rate of reaction is equal to the reverse rate of reaction ($\Delta G = 0$) and:

$$0 = \Delta G^{\circ} + RT \ln \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right] = \Delta G^{\circ} + RT \ln [K_{eq}]$$

$$K_{eq} = \exp\left(\frac{-\Delta G^{\circ}}{RT}\right)$$

⇒ **Activation Energy** - E_A - energy required to bring compounds to a reactive state. For example, energy may be required to break bonds in the molecules before they can react.

⇒ **The Electron Tower**

Half reactions are arranged so the couples with the most negative reduction potentials are at the top of the table and the most positive reduction potentials are at the bottom. All half reactions are shown as reductions. This arrangement can be thought of as an electron tower. Compounds at the top of the tower are good electron donors and compounds at the top are good electron acceptors. The greater the difference in potential between two half reactions in the tower, the greater the amount of energy from the reaction.

Enzymes

Activation Energy - E_A - energy required to bring compounds to a reactive state. For example, energy may be required to break bonds in the molecules before they can react.

Biological Catalysts - substance that lowers activation energy - substance is not changed in the process

Proteins twisted and folded into a specific shape - lock and key analogy.

Increases reaction rate $10^8 - 10^{20}$ times

Places strain on bonds to reduce E_A

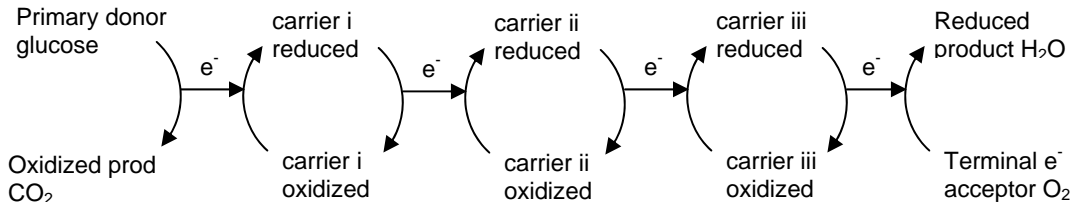
⇒ Mathematical expression for enzyme kinetics

- $[E] + [S] \rightleftharpoons [ES] \Rightarrow [P]$
- where E = enzyme, S = substrate, ES = Enzyme substrate complex, P = product
- From a mass balance on E we get:
- $$\frac{dP}{dt} = V_o = \frac{V_{\max}[S]}{K_m + [S]}$$
- where: V_{\max} = maximum rate of P production, K_m = half saturation constant
- Linweaver – Burke plot. Plot $1/V_o$ vs. $1/S$ and determine K_m and V_{\max}
- Note that these equations were developed for simple enzyme reactions. Enzyme reactions can be much more complex. In a cell many different enzymes are working and many different processes are occurring.

Microbial Metabolism

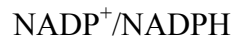
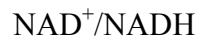
Electron carriers - series of oxidation reduction reactions

$\sum \Delta G = \Delta G$ for reaction between primary donor and terminal acceptor



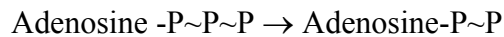
Kinds of carriers:

Freely diffusable -good electron donors



Membrane bound electron transport chain - flavoproteins, quinones, cytochromes

High energy phosphate carriers - The “energy coin” of the cell

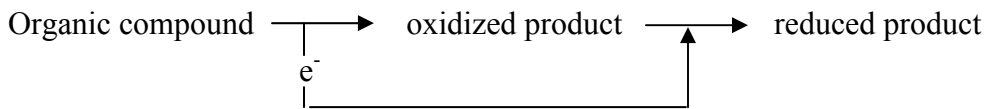


Two ways to make ATP

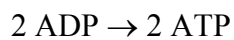
Substrate level phosphorylation - series of reactions with a substrate

Proton motive force - cell acts as a proton pump

Fermentation - only substrate level phosphorylation



Example: glucose \rightarrow 2 ethanol + 2 CO₂



Why do they do it?

No terminal electron acceptor around

Able to fill ecological niche

Products - yogurt, cheese, beer

Anaerobic treatment processes

Respiration

In the presence of O_2 , NO_3^- , SO_4^{2-} , Fe^{3+} or another terminal electron acceptor, the carbon source can be completely oxidized to CO_2 through:

Tricarboxylic acid cycle (TCA cycle)

Proton motive force

TCA cycle - complete oxidation of one mole of glucose to CO_2 and H_2O

1. Glycolysis: glucose \rightarrow 2 pyruvate + 2 ATP + 2 NADH
2. Each pyruvate is decarboxylated to Acetyl-CoA + 1 NADH + 1 CO_2
3. Acetyl group of acetyl-CoA combines with oxalacetate to form citrate
4. Citrate goes through a series of reactions - oxalacetate is regenerated + 2 CO_2 + 3 NADH + 1 FADH + 1 ATP

(key intermediates in the TCA cycle - citrate, α -ketoglutarate, succinate, oxalacetate)

Proton Motive force

Electrons from NADH are passed off to the electron transport chain used to pump H^+ out of the cell.

ATPase - membrane bound enzyme catalyzes the reaction $ADP \rightarrow ATP$

Microbial Metabolism Review

1. Cell couples energy from oxidation reduction reactions
2. A first approximation for the energy available for a reaction can be obtained from ΔG°
 - a) Using free energy of formation method
 - b) Using Faraday's law
3. The electron tower - a useful tool to visualize the energy available from the rxn between an electron donor/electron acceptor pair
4. The transfer of electrons from a primary donor to a terminal acceptor involves intermediates called electron carriers
 - a) Freely diffusible NAD⁺/NADH
 - b) Membrane bound electron transport chain
5. Cells need ATP to carry out biosynthesis and other cell functions
6. Cells make ATP two ways:
 - a) Substrate level phosphorylation - substrate goes through a biochemical pathway in which ATP is made
 - b) Proton motive force - H⁺ is pumped out of the cell to create a gradient - some of this potential energy is given up and ATP is formed through the action of ATPase.
7. Fermentation - a way for heterotrophs to make ATP in the absence of a terminal electron acceptor. Not much ATP is made. High energy waste products are produced.
8. Respiration - if a terminal electron acceptor is available organism can use both substrate level phosphorylation and proton motive force to generate ATP. Central metabolic cycle is TCA (citric acid) cycle.

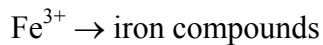
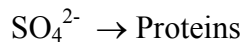
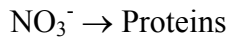
Alternate Modes of Energy Metabolism

If no O_2 is present, other oxidized compounds can serve as terminal electron acceptors for heterotrophic metabolism.

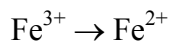
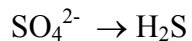
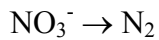
Anoxic Respiration - uses TCA cycle to oxidize organic carbon and reduce NAD^+ to $NADH$

Definitions

Assimilatory Reduction



Dissimilatory reduction



Denitrification

- Reaction is less energetically favorable than aerobic respiration
- Mostly carried out by facultative bacteria
- Reaction can also produce N_2O and NO
- Used in wastewater treatment, drinking water treatment, air pollution control
- Implications for soil fertility

Sulfate Reduction

- Organisms can use fermentation end products such as ethanol and pyruvate as electron donors
- First step in sulfate reduction requires ATP
- Alkalinity produced and metal sulfide production can be used to remediate acid mine drainage (AMD) sites - bioreactors or wetlands treatment.
- H_2S - highly odorous compound - sewer gas - reacts with Fe to produce black FeS

Iron Reduction

- Fe^{3+} is common in soil and rock
- Plays significant role in natural attenuation of hydrocarbons
- Fe^{2+} significant groundwater contaminant

Other Elements: Mn, Se, As

Organic electron acceptors

- Reductive dehalogenation - significant in clean up of sites contaminated with chlorinated hydrocarbons

Development of TEAP zones

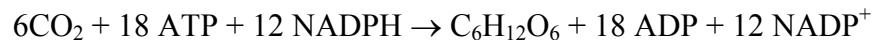
Terminal Electron Accepting Process

From Atlas and Bartha, 1998: Microorganisms within the community use the specific electron acceptor they are genetically capable of using that yields the maximal energy yield from the available substrate. Each electron acceptor is utilized at different redox potentials. This seemingly intelligent decision is in part due to metabolic regulation within a single population, and in part due to the inevitable outcome of competition between populations with diverse metabolic capabilities.

Chemolithotrophic Metabolism

- Energy from oxidation of inorganic compounds - H_2S , NH_3 , NO_2^- , Fe^{2+}
- Carbon from CO_2 - autotrophs
- Important role in cycling Fe, S, N in the environment
- Important role in environmental engineering - nitrification, H_2S oxidation

CO_2 Fixation



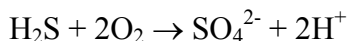
- Proceeds through a pathway called the Calvin cycle
- Requires a lot of energy in the form of ATP
- Requires a lot of reducing power in the form of NADPH

The problem for Chemolithotrophs - electrons can't run uphill without input of energy

$\text{NADP}^+/\text{NADPH}$	-0.32
$\text{SO}_4^{2-}/\text{H}_2\text{S}$	-0.22
$\frac{1}{2} \text{O}_2/\text{H}_2\text{O}$	+0.82

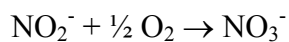
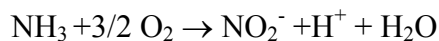
The solution - reverse electron transport

Sulfur Oxidizing Bacteria - importance in odor control through biofiltration, geochemical sulfur cycle, AMD generation:

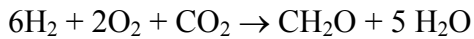


- Low energy yield
- Low growth rate
- Obligate aerobic bacteria
- Acidophiles

Nitrifying bacteria-importance in wastewater treatment, soil fertility, groundwater contamination:



Hydrogen bacteria- hydrogen is high enough on the electron tower, these organisms don't need reverse electron transport to generate reducing power. They can also use other electron acceptors, such as NO_3^- , ClO_4^- , SO_4^{2-}



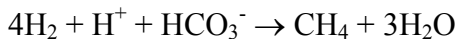
Fe oxidizing bacteria - important in AMD generation



Acetogenic bacteria - important role in anaerobic carbon cycle



Methanogens

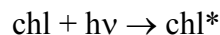


Fueling Reactions in Photosynthesis

Chlorophyll exists in 3 states:

Ground state chl

Excited state chl*



Oxidized state chl⁺

Photosystem I - Cyclic electron transport - used to make ATP

All occurs in the cell membrane with chl as both donor and acceptor

No electrons can be drawn off to produce reducing power

Three strategies for dealing with carbon in phototrophic organisms

1. Purple bacteria - photoheterotrophs - use organic carbon as carbon source, photosystem I as source of ATP. Large amount of reducing power not needed.
2. Green bacteria - anoxygenic photosynthesis uses reduced sulfur compounds and photosystem I to make NADPH - fixes inorganic C
3. Cyanobacteria, algae, green plants - oxygenic photosynthesis - 2 photosystems. Gets electrons by oxidizing H_2O to O_2 . Water is a very poor reducing agent but readily available. The use of two photosystems increases the potential enough to produce NADPH.