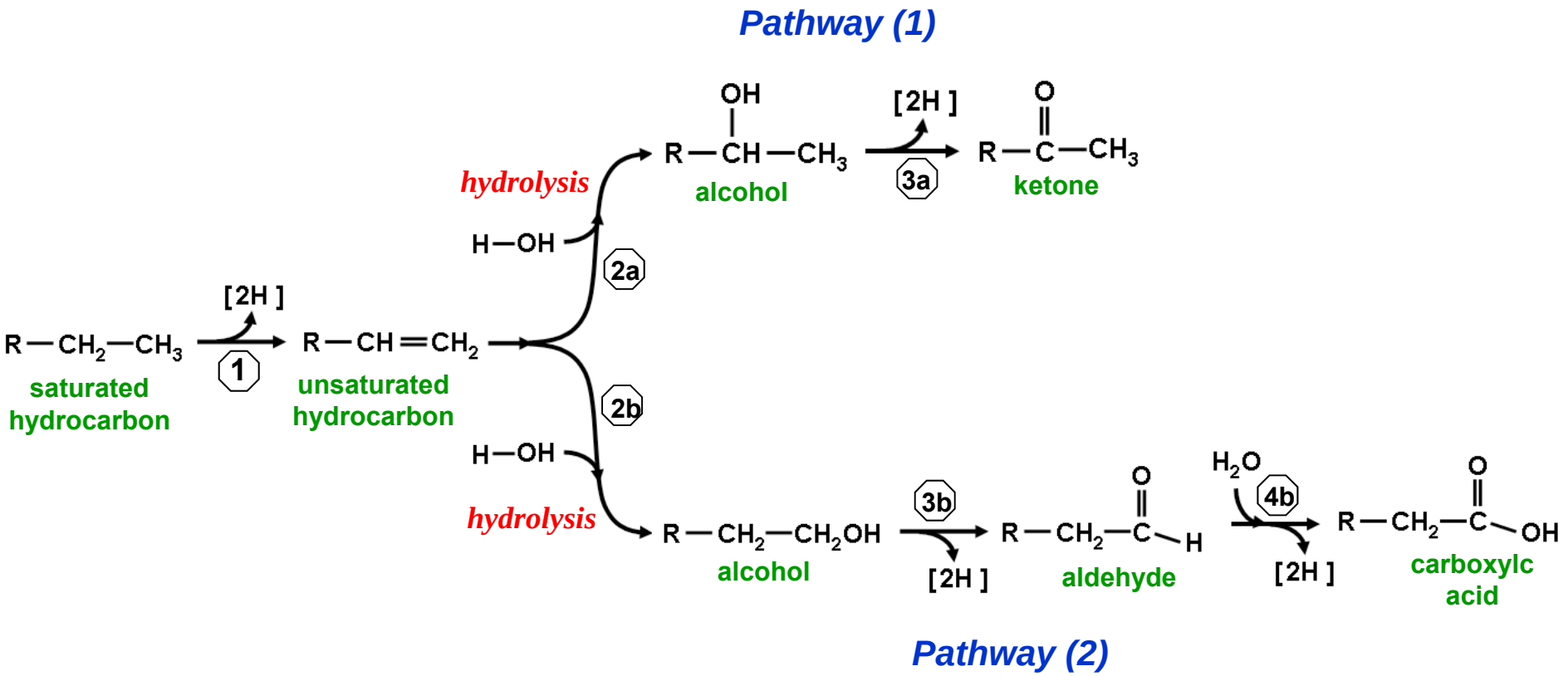
BIO 311C
Spring 2010

If you have a concern about the way Exam 1 or Exam 2 were graded, please set up an appointment to see Rebecca before 4:00 p.m. tomorrow (Tuesday 30 March).

Lecture 24 – Monday 29 Mar.

Example

Oxidation of a Hydrocarbon



With respect to a saturated hydrocarbon:

- **hydrocarbons with a single double bond, and alcohols, are 2 units more oxidized,**
- **aldehydes and ketones are 4 units more oxidized,**
- **carboxylic acids are 6 units more oxidized.**

More details of some of the individual reactions of these pathways are shown in the following four presentation slides.

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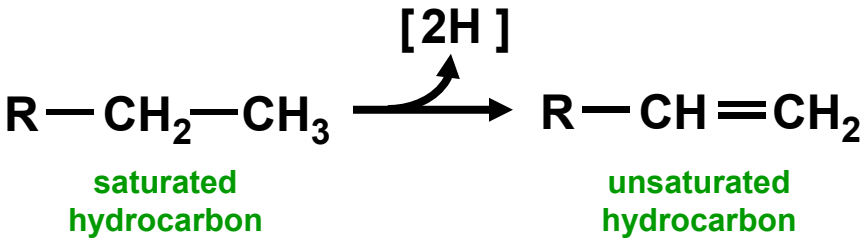
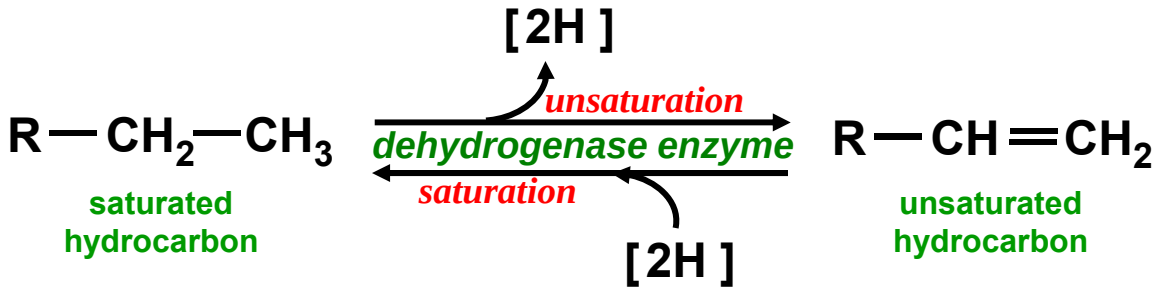
example

Reaction 1

Unsaturation of a Saturated Hydrocarbon



This half-reaction could be written to show more detail, as:



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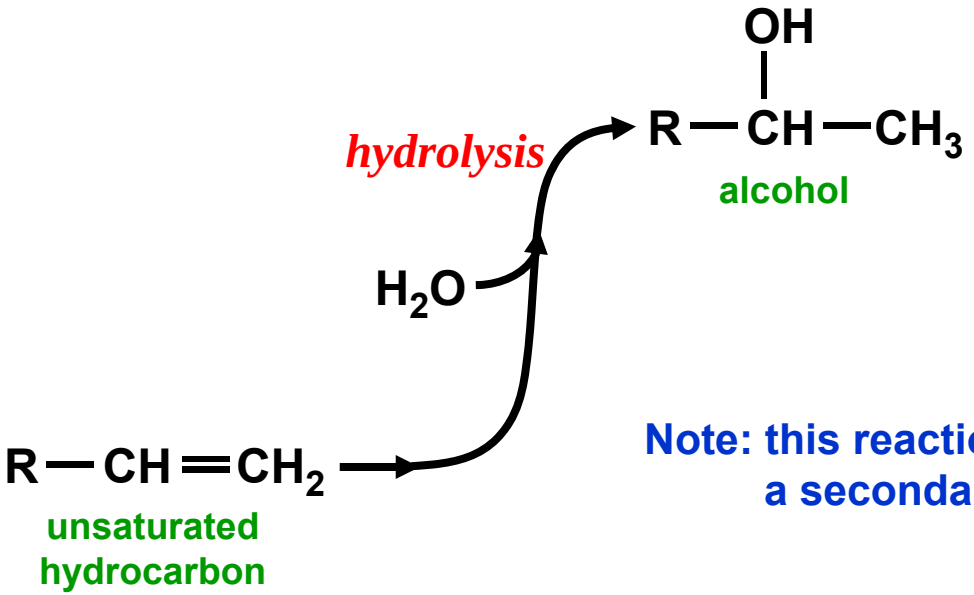
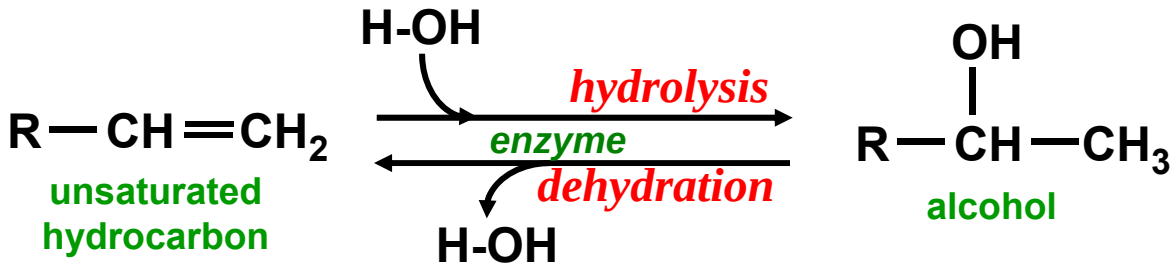
example

Hydrolysis of an Unsaturated Hydrocarbon



Note: this reaction produces a secondary alcohol

This reaction may be written to show more detail as:



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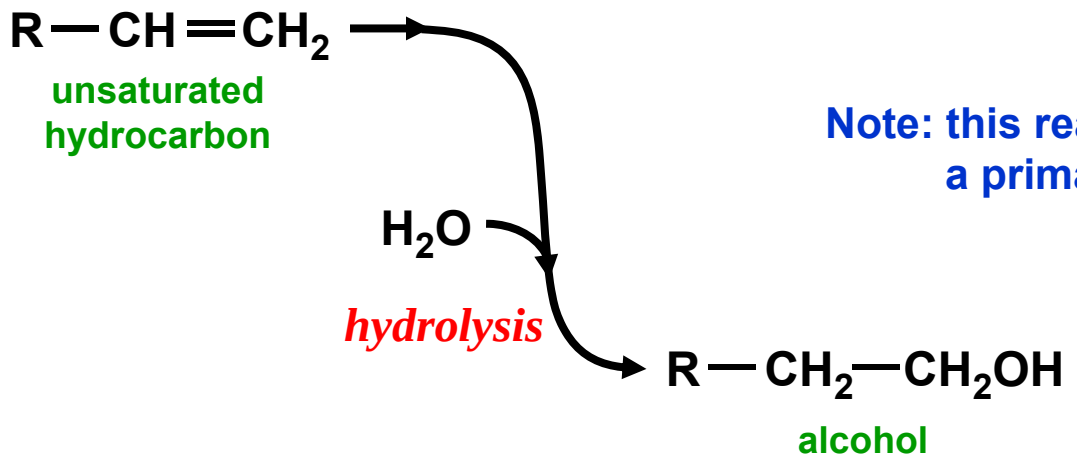
example

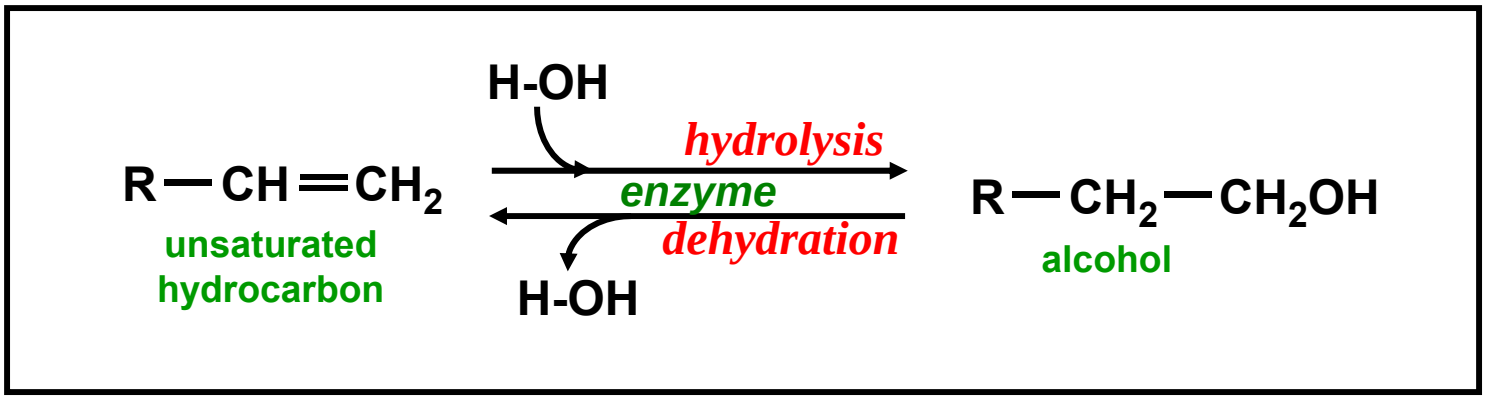
Reaction 2b

Hydrolysis of an Unsaturated Hydrocarbon



Note: this reaction produces a primary alcohol

This reaction may be written to show more detail as:



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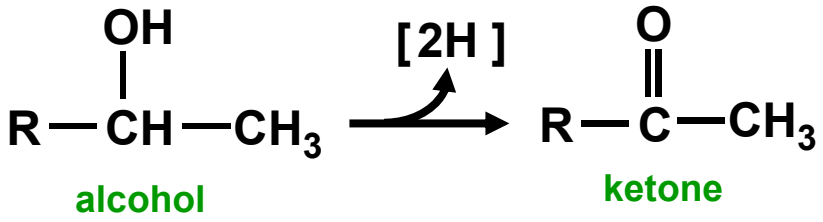
example

Oxidation of an Alcohol

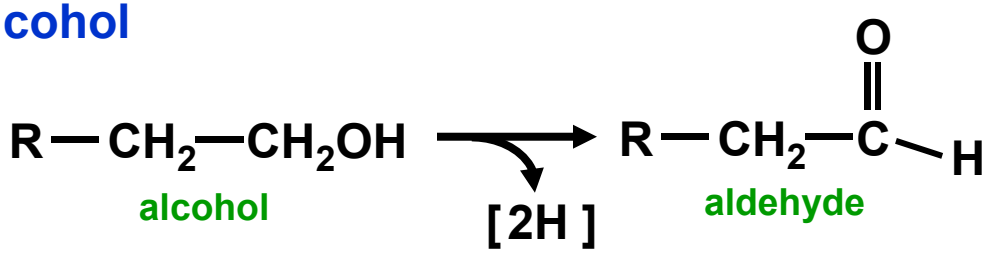
Oxidation of a secondary alcohol

Reaction 2a



Oxidation of a primary alcohol

Reaction 2b



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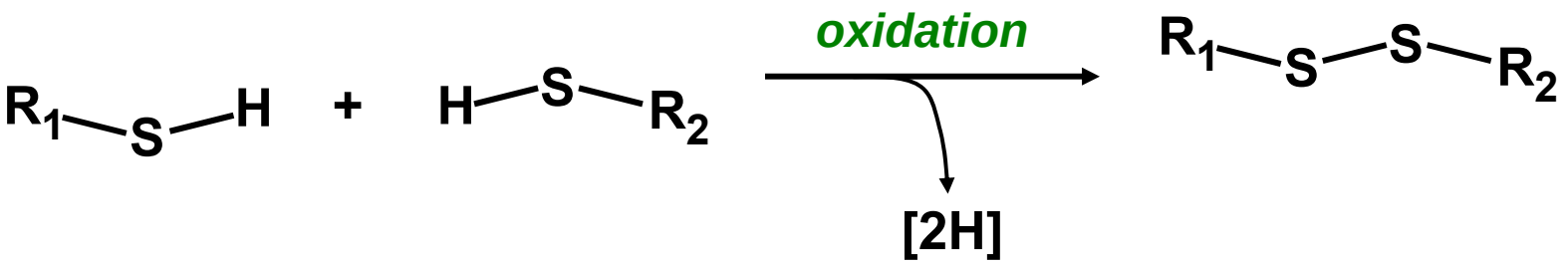
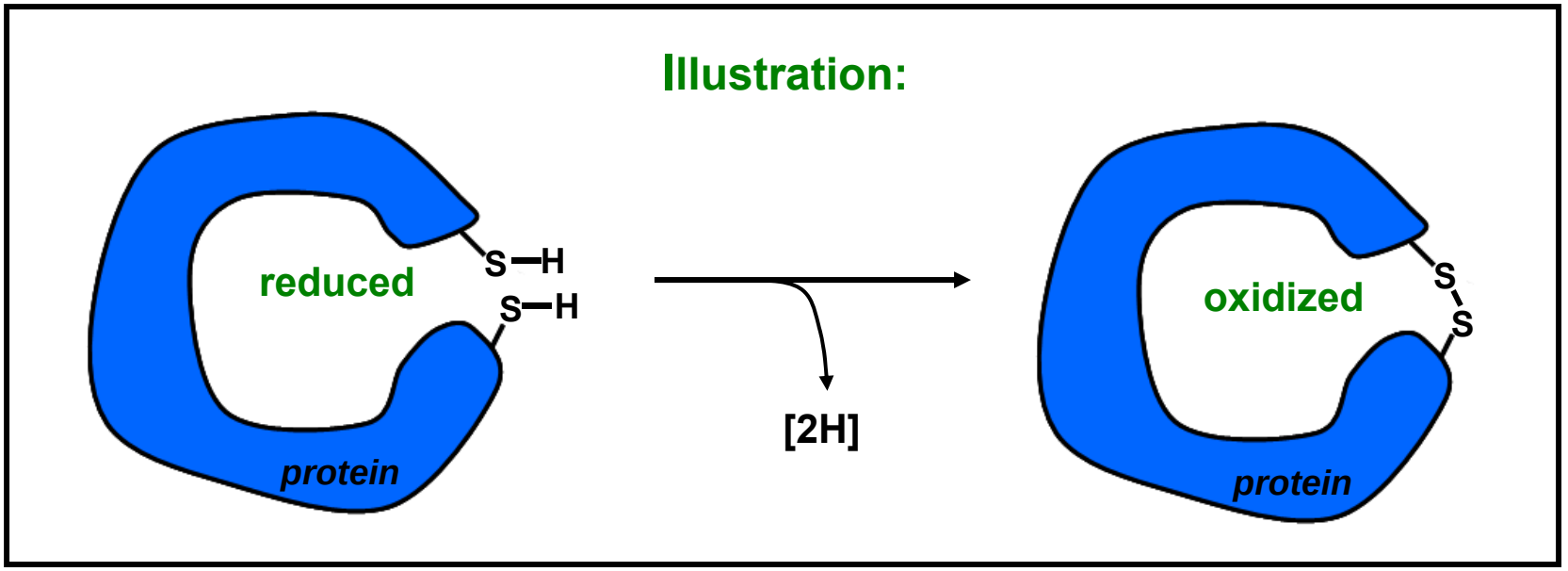
Oxidation of Two Sulfhydryl Functional Groups to Form a Disulfide





Disulfide bonds are important for stabilizing the tertiary structures of many proteins.

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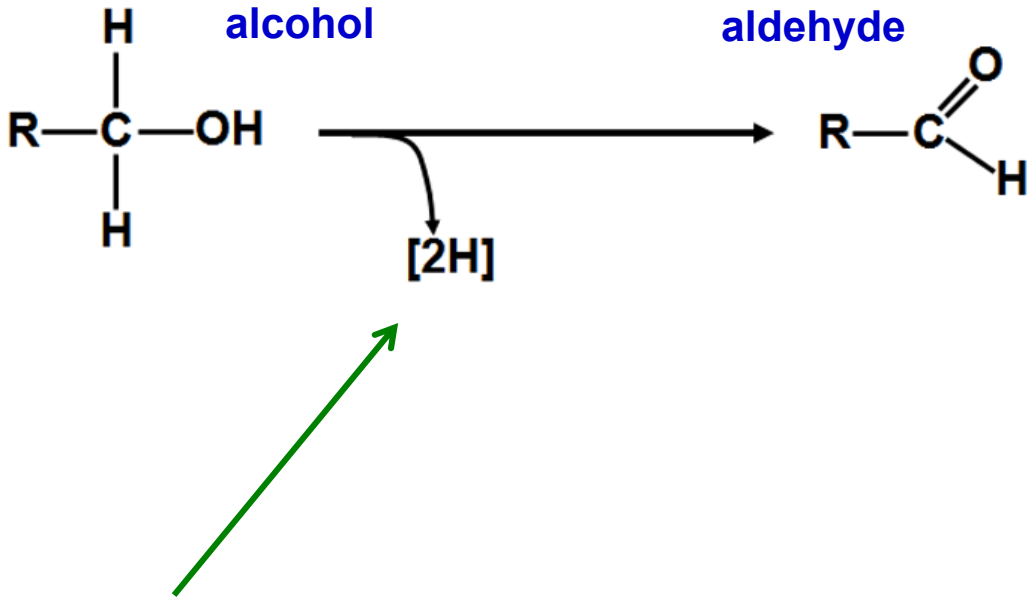
A Half-reaction, Showing the Oxidation of an Alcohol as a Pair of Hydrogen Atoms is Released.

Oxidation of an alcohol to an aldehyde (a half-reaction)



Hydrogen atoms are very unstable and reactive, and must immediately combine with something else.

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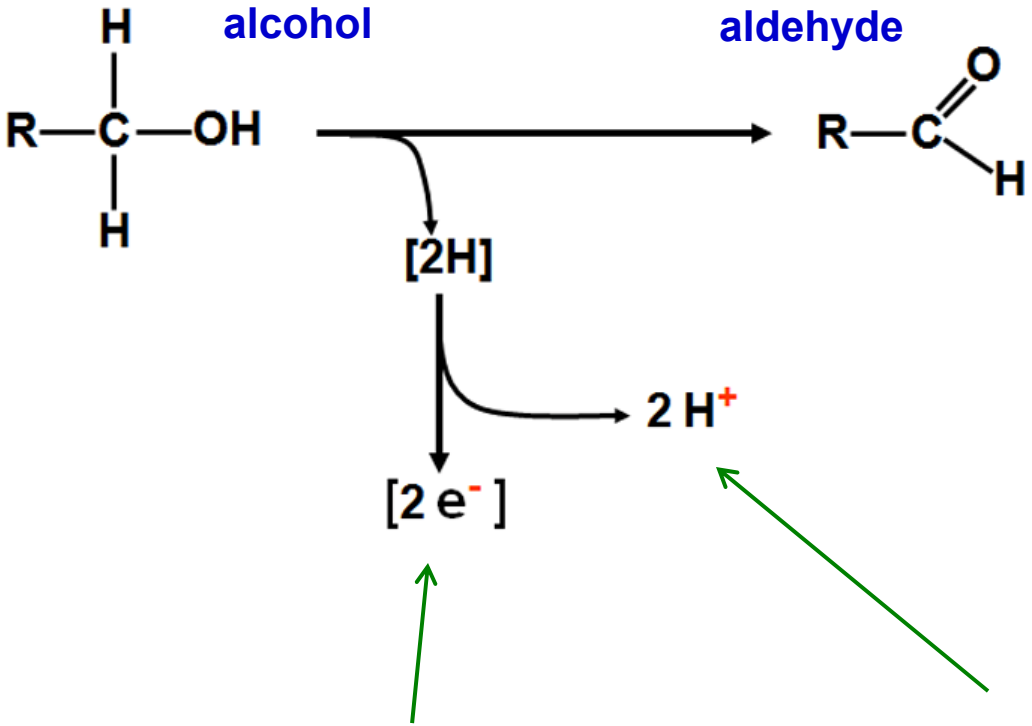
The Same Half- reaction Showing Hydrogen Atoms as Protons and Lone Electrons



Each hydrogen atom can lose its electron to become a proton (H^+).

Protons and electrons are very unstable and reactive, and therefore each must immediately combine with something else.

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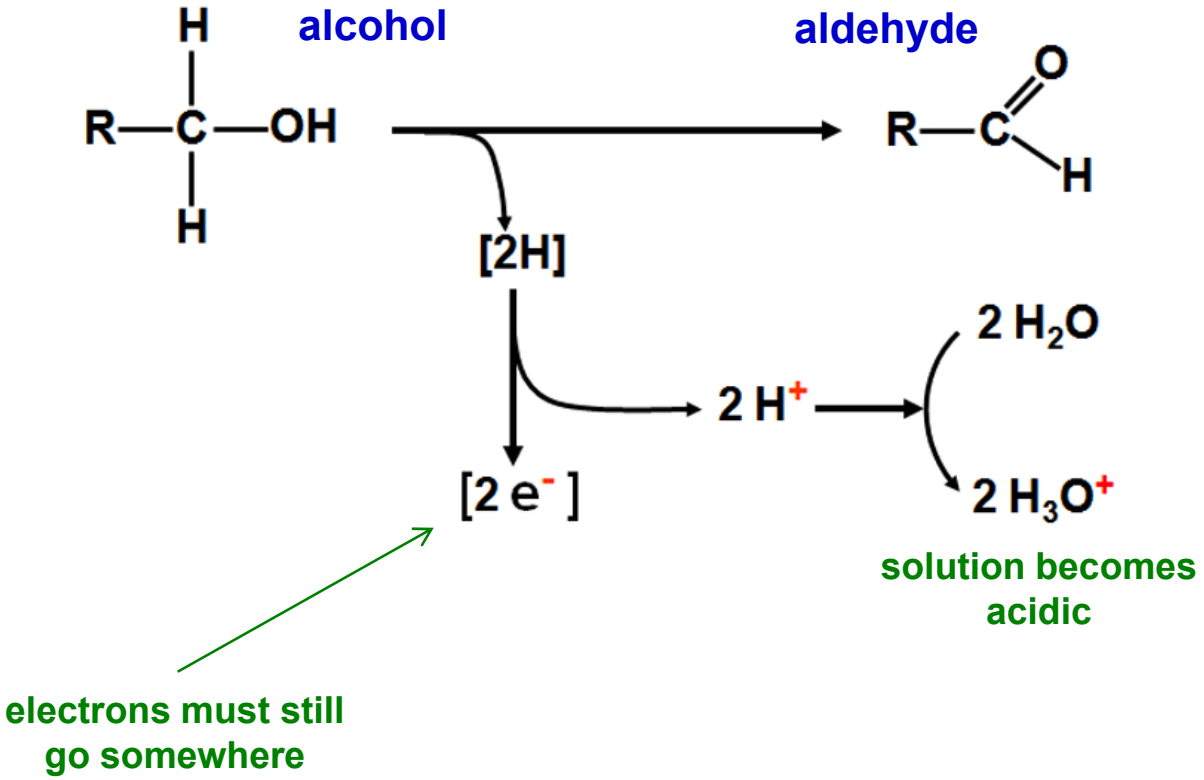
Protons Released During a Reaction that Occurs in an Aqueous Solution Immediately Protonate Water



Note: Some oxidation and reduction half-reactions utilize entire hydrogen atoms while others utilize only the electrons.

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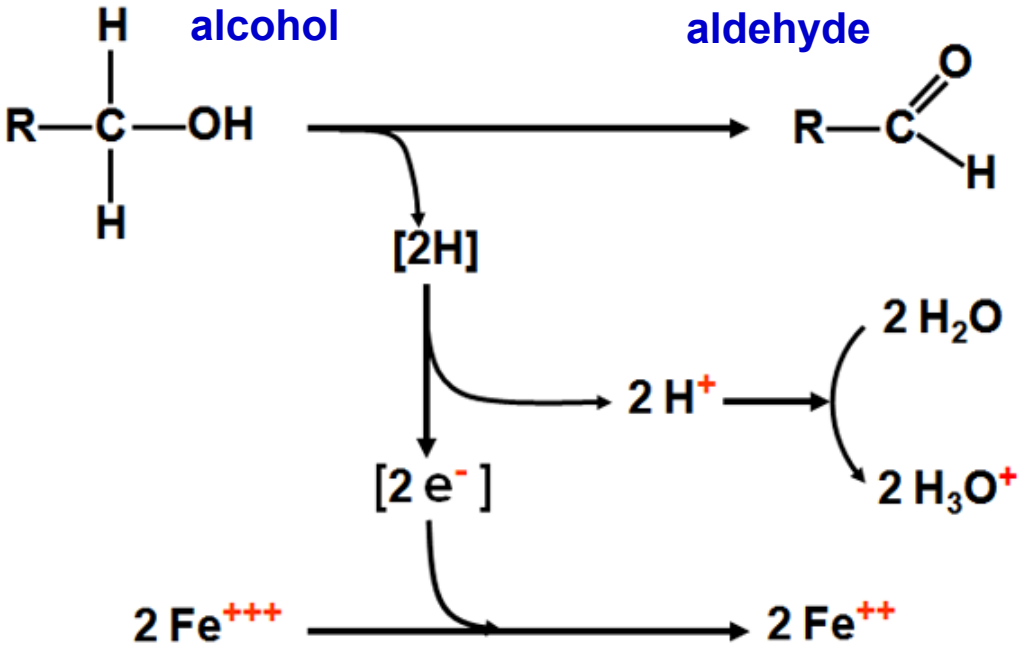
Electrons released in an alcohol oxidation half-reaction can reduce an inorganic ion



Reduction of ferric ions to ferrous ions (a half-reaction)

2 ferric ions

2 ferrous ions

Reactants of this oxidation/reduction reaction are alcohol, water and ferric ions.
Products of this reaction are aldehyde, hydronium ions (H_3O^+) and ferrous ions.

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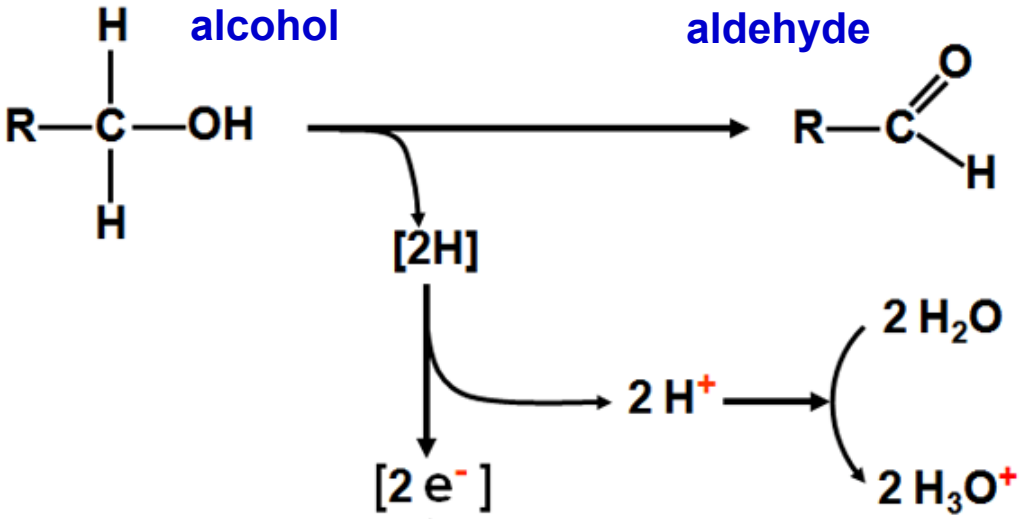
Summary of Last 4 slides: A Redox* Reaction in which an Alcohol is Oxidized as an Inorganic Ion is Reduced.

Oxidation of an alcohol (a half-reaction)



Reduction of ferric ions (a half-reaction)

$2\,Fe^{+++} \longrightarrow 2\,Fe^{++}$

2 ferric ions

2 ferrous ions

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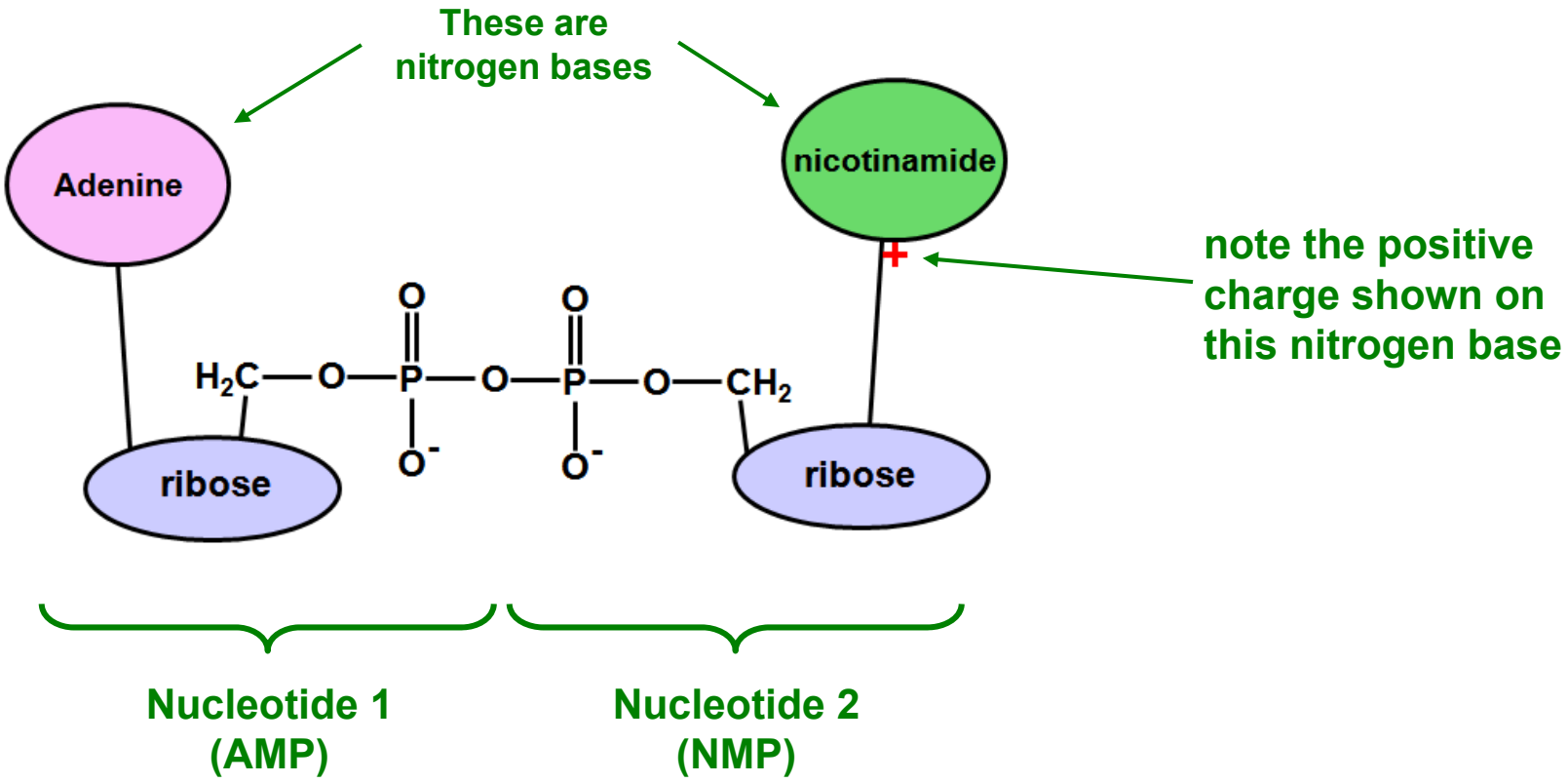
net reaction

$$R\text{-}CH_2OH + 2\,Fe^{3+} + 2\,H_2O \longrightarrow R\text{-}CHO + 2\,Fe^{2+} + 2\,H_30^{+}$$

*Oxidation/reduction reactions are often called redox reactions. *

Abbreviated Structure of NAD^+, a dinucleotide that is an important hydrogen-atom carrier in cells



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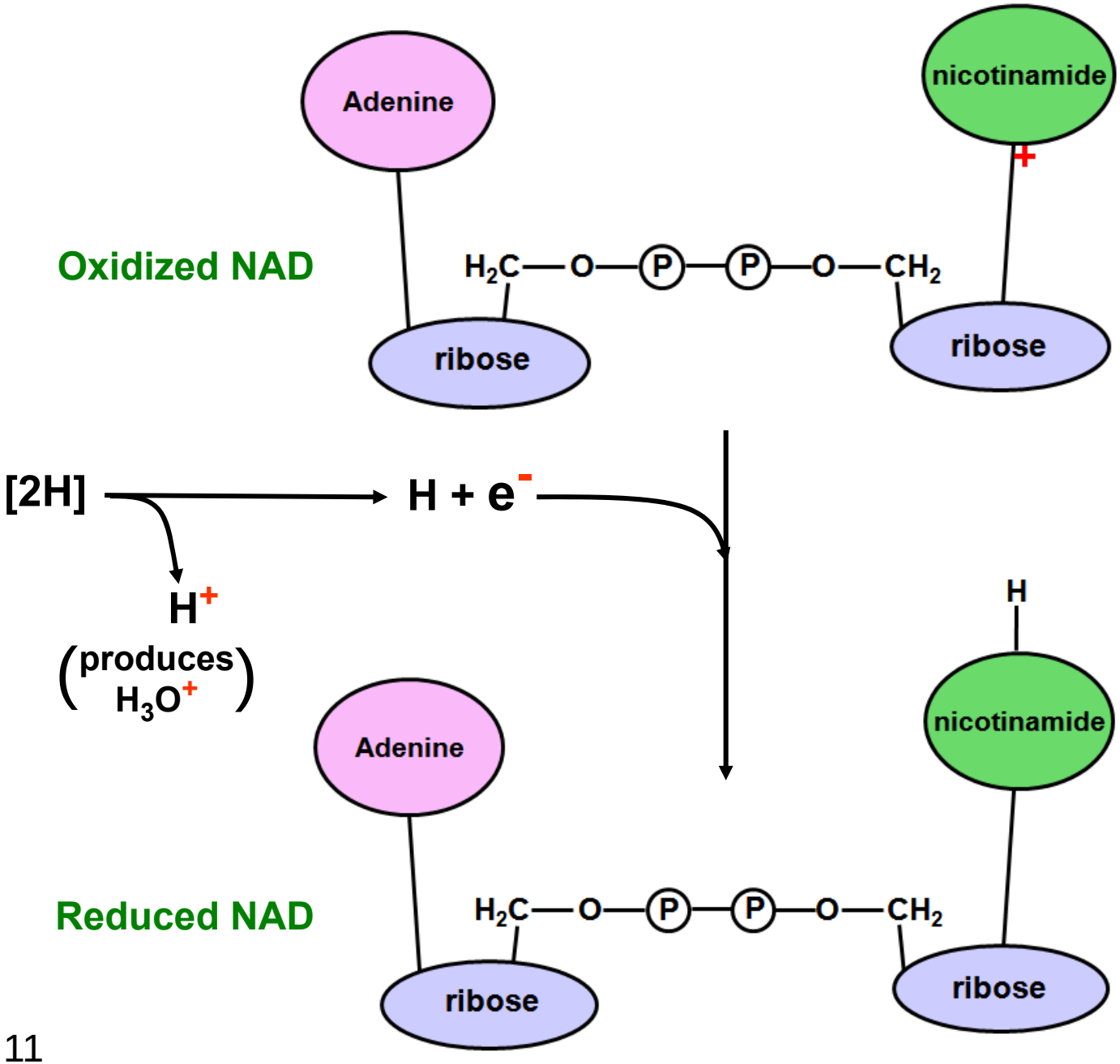
Reduction of NAD^+



Net half-reaction:

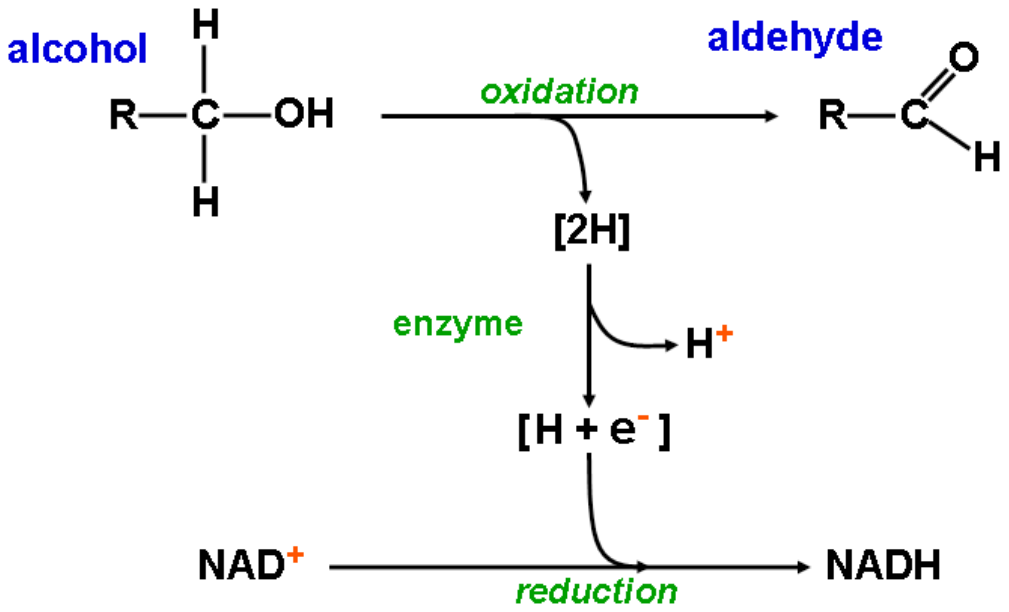
$NAD^+ + [2H]$

↓

$NADH + H^+$

*

Typical Reaction Involving the Reduction of NAD^+



(half-reaction)
oxidation of an alcohol

(half-reaction)
reduction of NAD^+

Net reaction as usually shown:

$$R\text{-}CH_2OH + NAD^+ \xrightarrow{dehydrogenase} R\text{-}CHO + NADH + H^+$$

In practice, the H^+ product would combine with water to produce H_3O^+.

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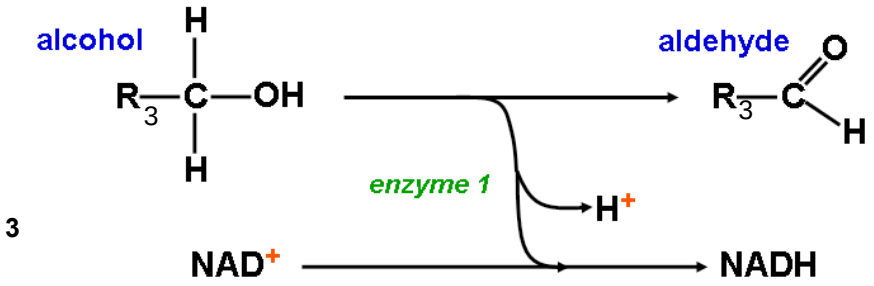
NAD^+ acts as a carrier of reducing units in living cells.

Example:

Reaction 1 (oxidation of an alcohol)



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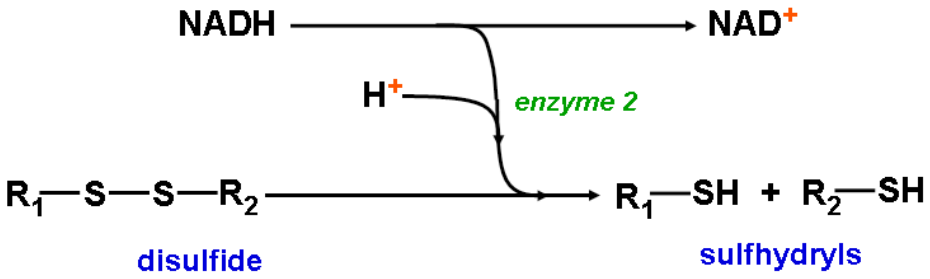
Reaction 2 (reduction of a disulfide)



NAD^+ acquires two reducing units in Reaction 1.

NADH donates two reducing units in Reaction 2.

Sum of the Reactions 1 and 2:

$$R_3CH_2OH + R_1\text{-}S\text{-}S\text{-}R_2 \longrightarrow R_3CHO + R_1\text{-}SH + R_2SH$$

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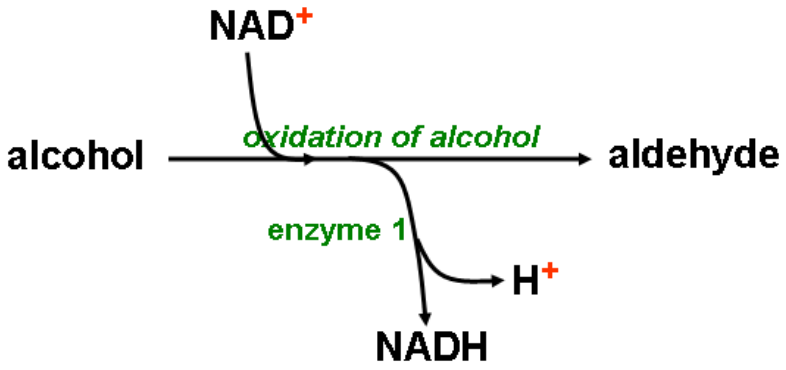
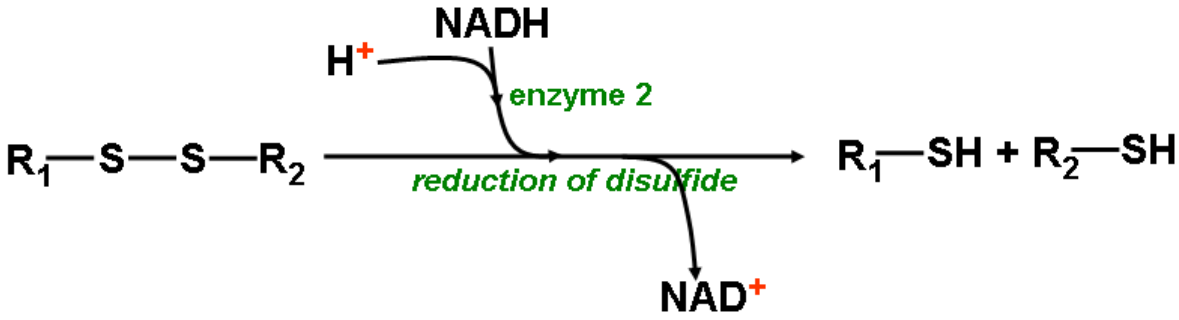
Reactions 1 and 2 from the Previous Presentation Slide, Shown in a Slightly Different Way

Reaction 1 (oxidation of an alcohol)



Reaction 2 (reduction of a disulfide)



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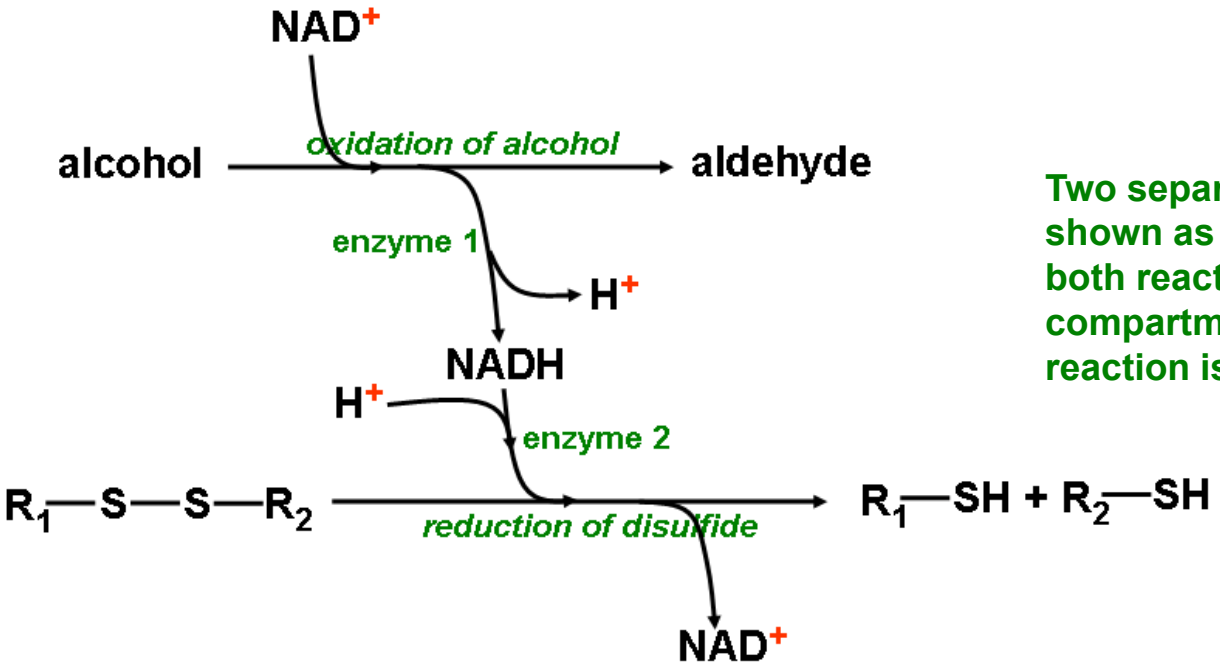
Reactions 1 and 2 from the Previous Presentation Slide, Shown as One Continuous Process

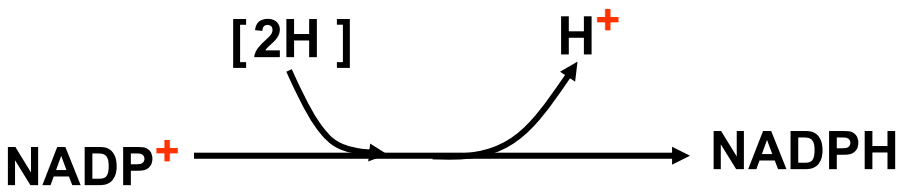


Two separate metabolic reactions can be shown as one continuous process when both reactions occur in one compartment and a product of one reaction is a reactant the other reaction.

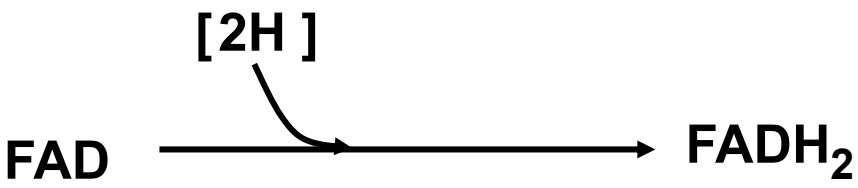
net: alcohol + R_1-S-S-R_2 $\xrightarrow{\textit{enz. 1, enz. 2}}$ aldehyde + R_1-SH + R_2-SH

An alcohol is oxidized and a disulfide is reduced in a two-reaction process. *

Other Important Hydrogen-atom Carriers in Cells



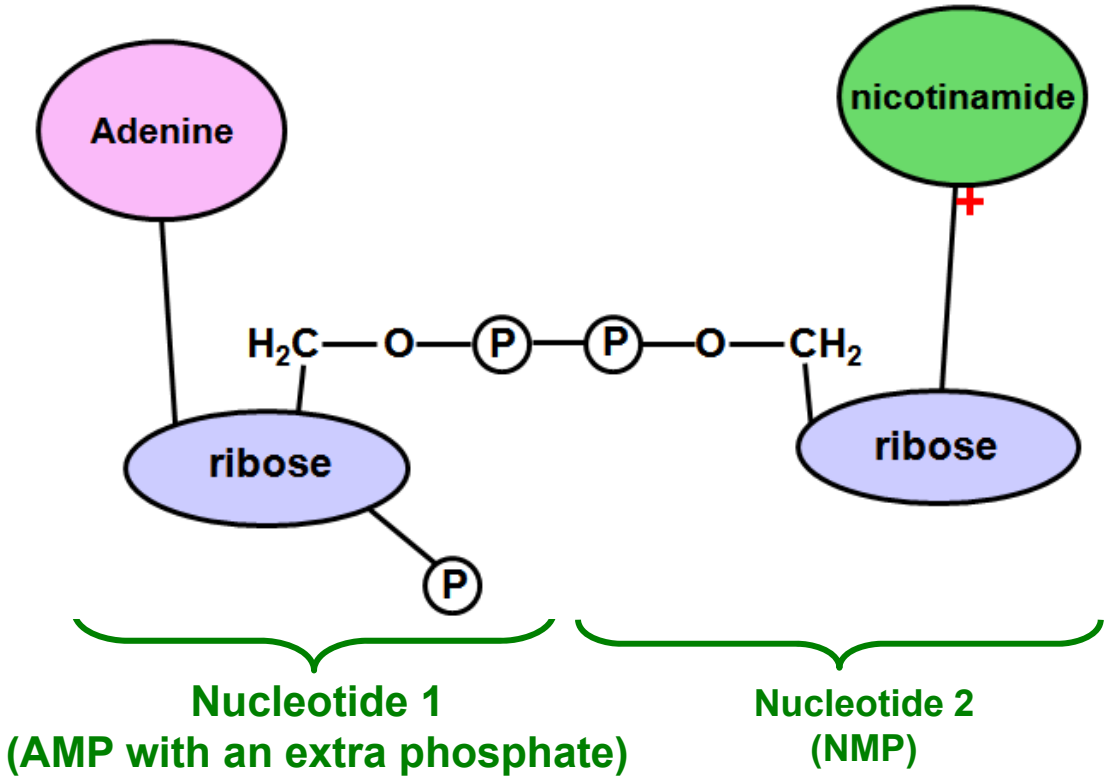
Half-reaction: $NADP^+ + [\ 2H\ ] \rightleftharpoons NADPH + H^+$



Half-reaction: $FAD + [\ 2H\ ] \rightleftharpoons FADH_2$

*

Structure of $NADP^+$



The extra phosphate on $NADP^+$ allows each enzyme that catalyzes a redox reaction to distinguish $NADP^+$ from NAD^+(which doesn't carry the extra phosphate). Thus NAD^+ and $NADP^+$ can function in distinct metabolic reactions, even though they may occur in the same cellular compartment and function by the same mechanism.

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Requirements of Metabolic Reactions

- Each reaction must proceed in the right direction; i.e. the reaction must have a negative ΔG value in order to proceed in the forward direction.

- Each reaction must have an available pathway (for most metabolic reactions a mechanism that uses an enzyme) in order to proceed at all.

- The rate and extent of each reaction must be carefully controlled.

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Four levels of organization of the metabolism of a living cell

1. Individual metabolic reactions
2. Metabolic pathways
3. Metabolic systems*
4. Metabolism collectively within the cell

Cellular metabolism is regulated at each of these levels of organization.

*A metabolic system is a set of two or more metabolic pathways in a cell that have some relationship to each other.

*

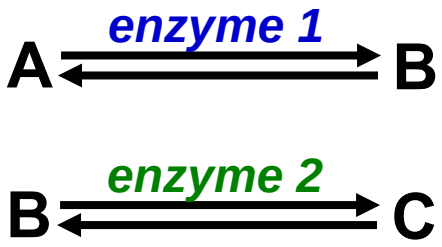
Definitions:

A metabolic pathway is a set of sequentially connected metabolic reactions that all occur within the same compartment of a cell.

A "set of sequentially connected reactions" is two or more reactions, such that a product of the first reaction serves as a reactant of the second reaction, a product of the second reaction serves as a reactant of the third reaction, etc.

Two sequentially connected reactions that occur in the same compartment are said to be coupled together. Thus a metabolic pathway consists of a series of coupled reactions.

Example:
B is a product on one reaction and a reactant of the other.



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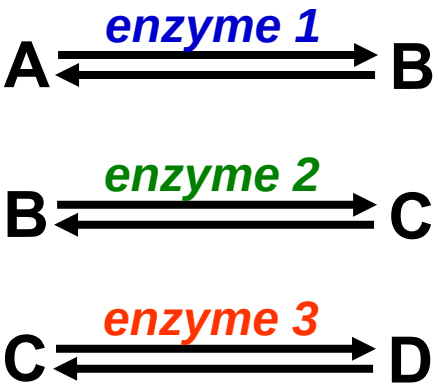
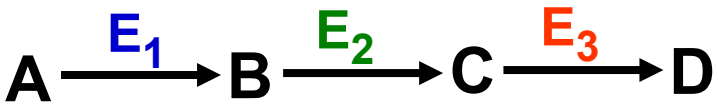
Ways to Show a Metabolic Pathway That Consists of Three Metabolic Reactions



Individual metabolic reactions may be shown separately.



Reactions may be shown coupled together by writing intermediate substrates once only. Often the reverse arrow is not shown. Sometimes the name of the enzyme is abbreviated.

The entire metabolic pathway may be abbreviated by showing only initial reactant(s) and final product(s), illustrated as a single reaction. Sometimes the name of the metabolic pathway is written above or below the arrow.

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