

BIOC 384: M05.T05-Miesfeld

Assigned Reading: *Biochemistry* Chapter 7.2b



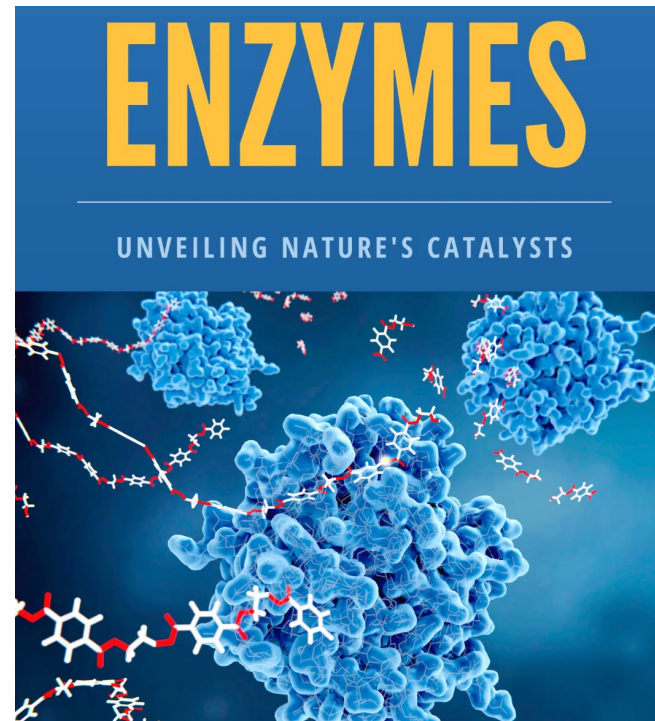


Enzyme-Mediated Chemical Reactions in Cells



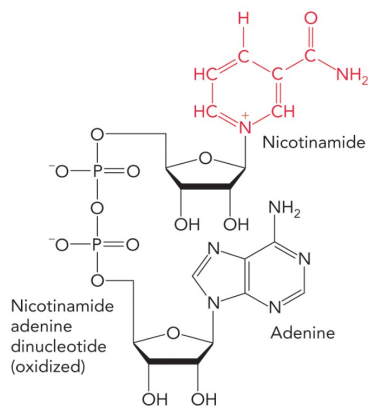
The Big Picture

- Enzyme-mediated chemical catalysis in *living systems* fall into three broad categories of biochemical reactions: redox reactions, metabolite transformations, and reversible covalent modifications.
- Enzymes ensure that chemical catalysis occurs rapidly and specifically, enabling the responsive nature of living systems.

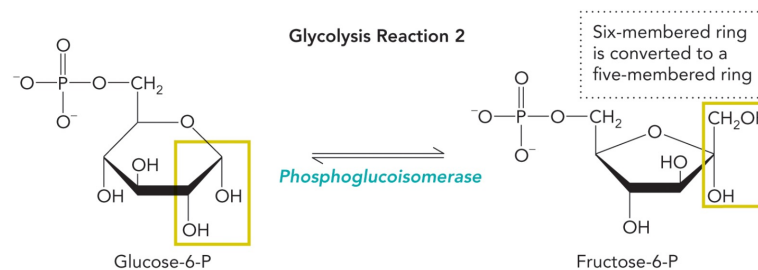


Enzyme-Mediated Reactions Inside Cells

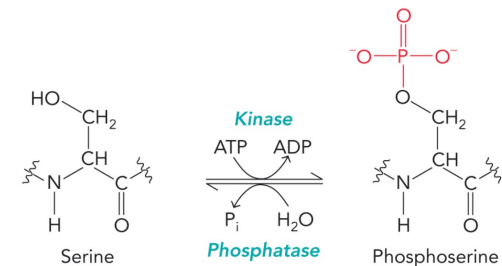
- There are three categories of enzyme-mediated chemical catalysis in cells:
 - **Coenzyme-dependent** redox reactions for energy conversion
 - **Metabolite transformation** reactions for biosynthesis and degradation
 - **Reversible covalent modifications** for regulation and signaling



Coenzyme-dependent



Metabolite transformation

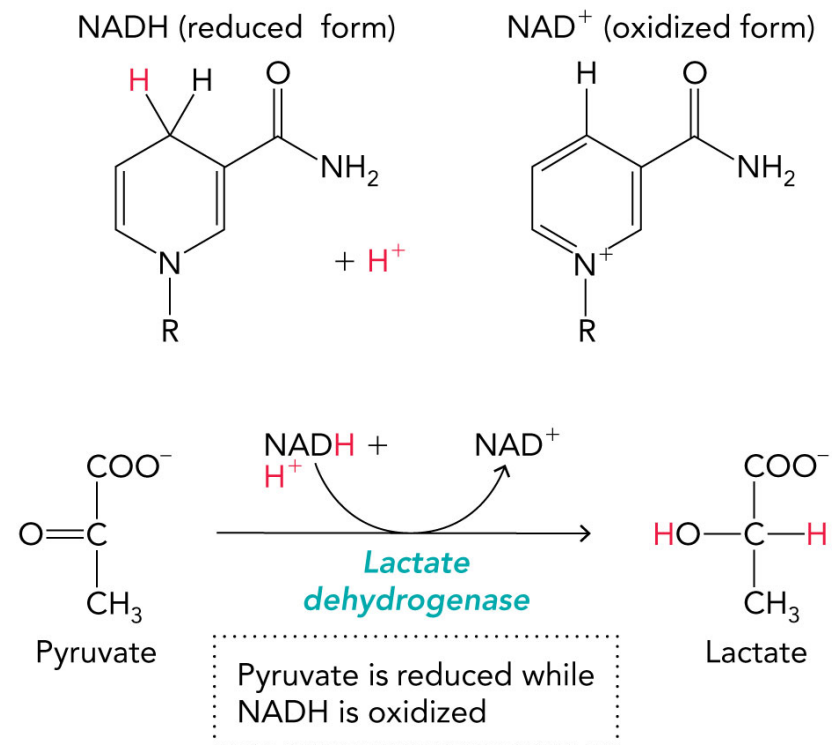


Reversible covalent modification



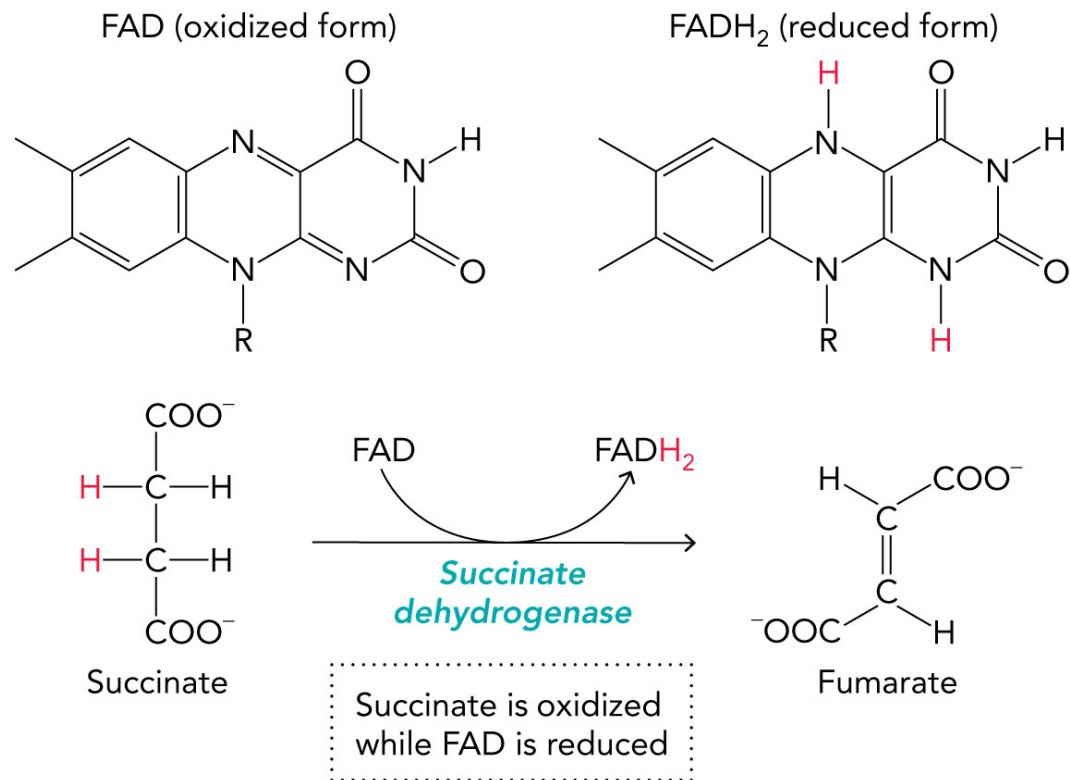
Coenzyme-Dependent Redox Reactions

- Redox reactions involve oxidation (electron loss) and reduction (electron gain); free electrons cannot exist stably in solution, so coenzymes mediate these transfers.
- Enzymes catalyze redox reactions essential for generating ATP and reducing equivalents in glycolysis, the citrate cycle, and oxidative phosphorylation.



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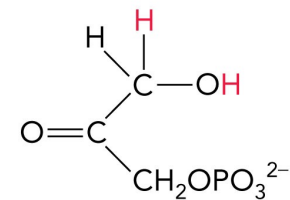


Metabolite Transformation Reactions

Isomerization Reactions:

- Isomerase enzymes catalyze rearrangements of atoms within a molecule without changing the molecular formula.
- Triose phosphate isomerase interconverts dihydroxyacetone phosphate (DHAP) and glyceraldehyde-3-phosphate (G3P).

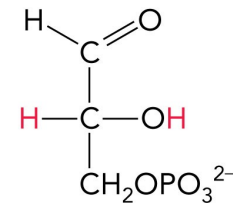
Isomerization reaction



Dihydroxyacetone
phosphate
(C₃H₇O₆P)



*Triose phosphate
isomerase*



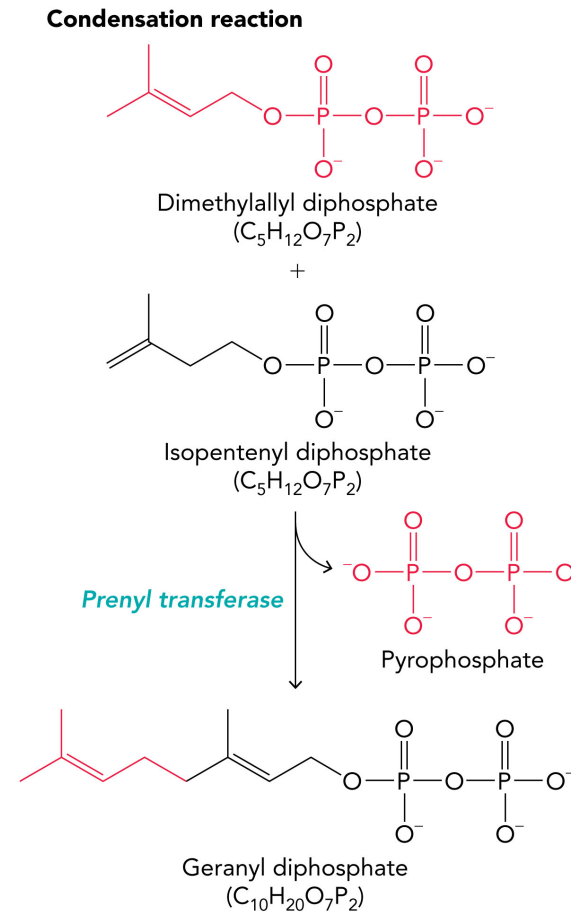
Glyceraldehyde-
3-phosphate
(C₃H₇O₆P)



Metabolite Transformation Reactions

Condensation Reactions:

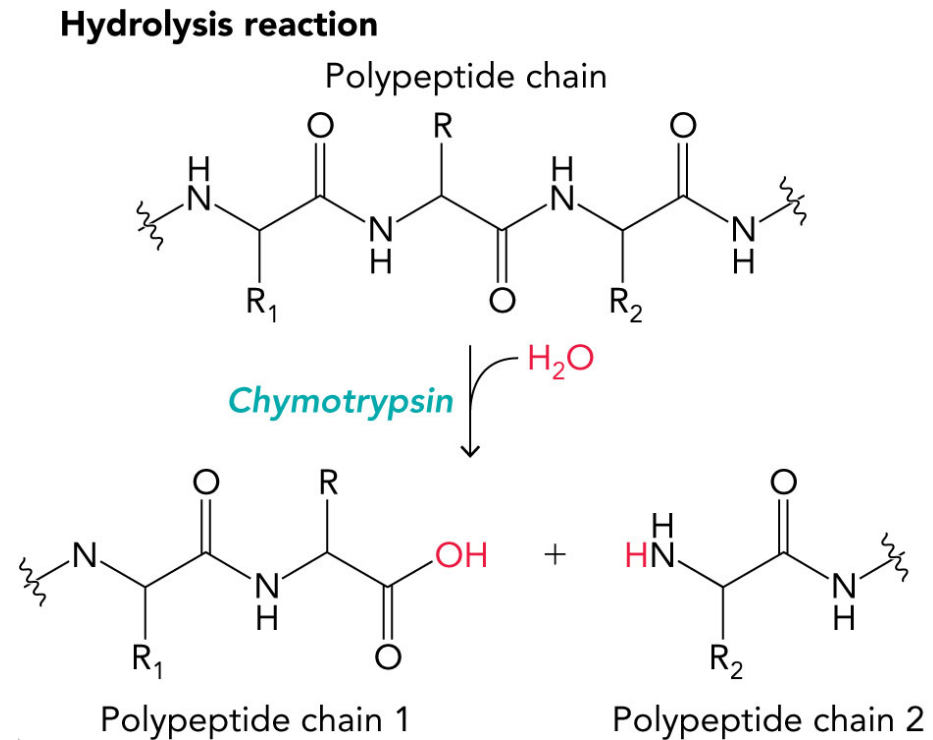
- Condensation reactions join two smaller molecules, often with loss of a small molecule (e.g., water or pyrophosphate).
- Prenyl transferase condenses dimethylallyl diphosphate and isopentenyl diphosphate to form geranyl diphosphate in cholesterol biosynthesis.



Metabolite Transformation Reactions

Hydrolysis and Dehydration Reactions:

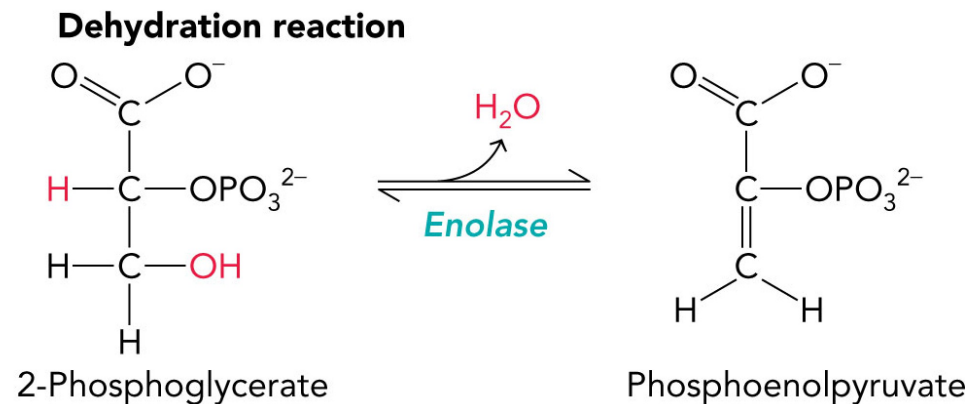
- Hydrolysis adds water to cleave bonds, while dehydration removes water to form new bonds.
- [Hydrolysis](#): Chymotrypsin uses water to cleave peptide bonds.
- [Dehydration](#): Enolase removes water from 2-phosphoglycerate to form phosphoenolpyruvate in glycolysis.



Metabolite Transformation Reactions

Hydrolysis and Dehydration Reactions:

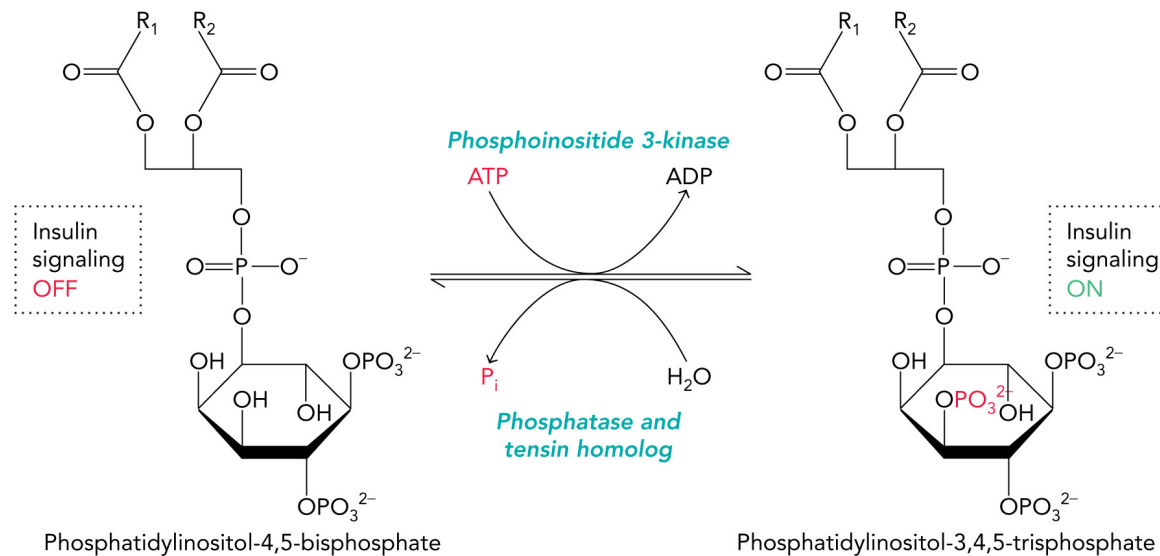
- Hydrolysis adds water to cleave bonds, while dehydration remove water to form new bonds.
- Hydrolysis: Chymotrypsin uses water to cleave peptide bonds.
- Dehydration: Enolase removes water from 2-phosphoglycerate to form phosphoenolpyruvate in glycolysis.



Reversible Covalent Modifications

Phosphorylation and Dephosphorylation:

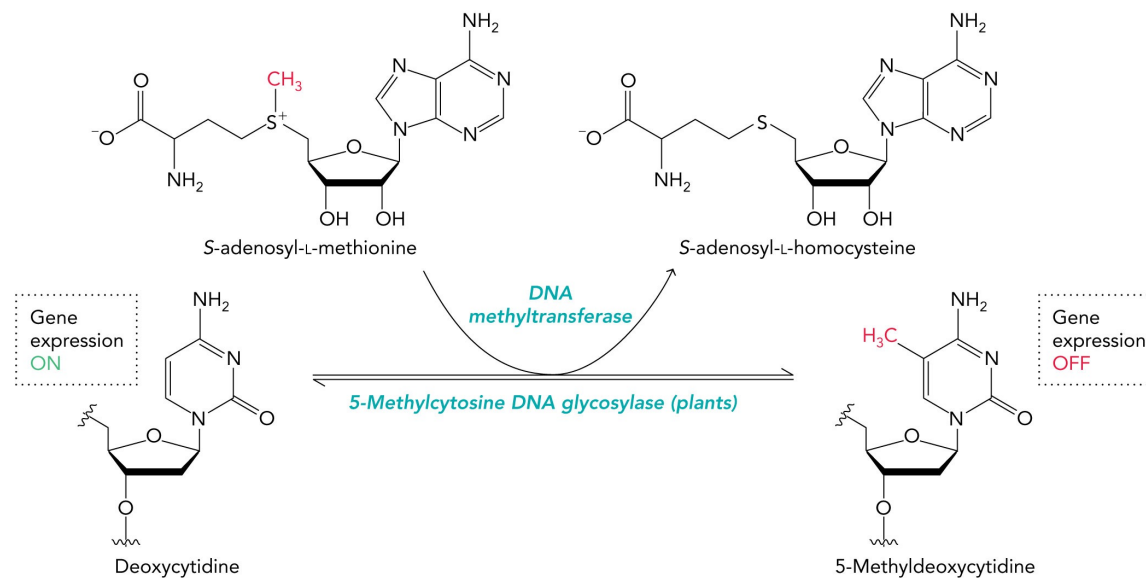
- Kinases transfer a phosphate from ATP to proteins (commonly Ser, Thr, or Tyr residues). Phosphatases remove the phosphate group via hydrolysis.
- Insulin signaling activates PI-3 Kinase, which phosphorylates membrane lipids. PTEN later removes these phosphates to terminate signaling.



Reversible Covalent Modifications

Methylation and Demethylation:

- DNA methyltransferases add methyl groups to cytosine bases using S-adenosyl-L-methionine, forming 5-methylcytosine, which represses gene transcription by recruiting silencing complexes.
- Demethylation reverses repression, reactivating gene expression.



Key Concepts to Guide Your Learning

- Coenzyme-dependent redox reactions in cells usually require coenzymes such as NAD^+/NADH or FAD/FADH_2 . These redox reactions most often involve the transfer of $2 e^-$, but can involve a $1 e^-$ transfer through a radical intermediate.
- Metabolite transformation reactions are found in metabolic pathways and most often involve isomerization reactions, condensation reactions, or hydrolysis or dehydration reactions.
- Reversible covalent modification reactions include the addition (kinases) and removal (phosphatases) of phosphoryl groups in biomolecules; another reversible covalent modification is methylation and demethylation of DNA.

