

# Chem 109 C Bioorganic Compounds 

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## Chapter 23: Coenzymes

Overview and Introduction:

- enzymes are biological catalysts
- many enzymes are inactive without cofactors
- cofactors are 1) metal ions or 2) coenzymes
- coenzymes - organic molecules, derived from vitamins



## Chapter 23: Coenzymes

| Coenzyme | Vitamin | Reaction catalyzed |
| :---: | :---: | :---: |
| NAD ${ }^{+}$, NADP ${ }^{+}$/ NADH, NADPH | niacin, nicotinamide | oxidation/reduction of alcohols |
| FAD / FADH ${ }_{2}$ | riboflavin (B2) | oxidation/reduction, other |
| Thiamine pyrophosphate TPP | thiamine (B1) | acyl group transfer |
| Lipoic acid /dihydropipoic acid | lipoic acid | oxidation/reduction |
| Coenzyme A, CoASH | pantothenic acid (B5) | acyl group transfer |
| Biotin | biotin (B7) | carboxylation |
| Pyridoxal phosphate PLP | pyridoxin (B6) | 6 amino acid reactions |
| Coenzyme $\mathrm{B}_{12}$ | vitamin B12 | isomerization |
| Tetrahydrofolic acid, THF | folic acid | one-carbon transfer |
| Vitamin $\mathrm{KH}_{2}$ | vitamin K | carboxylation |

## Chapter 23: Coenzymes

factors characterizing a coenzyme:

- chemical structure
- associated vitamin
- type of reaction catalyzed
- reaction mechanism
- dietary source
- associated disease


## NAD+-NADH, NADP+ ${ }^{+}$-NADPH



NAD ${ }^{+}$


NADH$\mathrm{NAD}^{+}$is a catabolic enzyme [NAD $\left.{ }^{+}\right] /[$NADH] ~ $1000: 1$ (cytosol) [ 0.3 mM ]


- catalyze redox (oxidation-reduction) reactions
- source of nicotinamide: meats, vegetables, peanuts etc.
- deficiency disease: pellagra (skin lesions, sensitivity to light etc.)


## NAD+-NADH, NADP+ ${ }^{+}$-NADPH



NADP ${ }^{+}$


NADPH

- NADP ${ }^{+}$is an anabolic enzyme[NADP+]/[NADPH] ~ 1 : 100
- catalyze redox (oxidation-reduction) reactions
- source of nicotinamide: meats, vegetables, peanuts etc.
- deficiency disease: pellagra (skin lesions, sensitivity to light etc.)


## NAD+ ${ }^{+}$NADP+

## Oxidation with NAD+ (or NADP ${ }^{+}$):



General mechanism of oxidation:




## $\mathbf{N A D}^{+}$, NADP ${ }^{+}$

## Oxidation with $\mathrm{NAD}^{+}$(or NADP ${ }^{+}$), examples:



- important reaction in the citric acid cycle


## NAD $^{+}$, NADP $^{+}$

## Reduction with NADH (or NADPH), a reverse process:



General mechanism of reduction:


- NADH and NADPH are $\mathrm{H}^{-}$donors


## NAD+ ${ }^{+}$NADP+

## Reduction with NADPH (or NADH), examples:



$\beta$-aspartate semialdehyde

homoserine

- important reaction in an anabolic pathway


## NAD $^{+}$, NADP $^{+}$

## Oxidation - a more complex example:



G3P






D-glyceraldehyde-3-phosphate
D-1,3-diphosphoglycerate







D-glyceraldehyde-3-phosphate
D-1,3-diphosphoglycerate


## Stereochemistry of enzymatic reactions: enzyme reactions are stereospecific




