Table 1.21 Vitamin B-complex and their coenzyme forms

Vitamin	*Coenzyme form*	*Reaction or process promoted*
Thiamine (B_1)	Thiamine pyrophosphate	Decarboxylation, aldehyde group transfer
Riboflavin (B_2)	FAD and FMN	Redox reaction
Pyridoxine (B_6)	Pyridoxal phosphate	Amino group transfer
Nicotinic acid (niacin)	NAD^+ and $NADP^+$	Redox reaction
Pantothenic acid (B_5)	Coenzyme A	Acyl group transfer
Biotin (vit - H)	Biocytin	Carboxylation (carboxylase)
Folic acid	Tetrahydrofolic acid	One-carbon group transfer
Vitamin B_{12}	Deoxyadenosylcobalamin	Intramolecular rearrangements (mutase,

The vitamins in the human diet that are coenzyme precursors are all water soluble vitamins.

Table 1.22 Example of some enzymes and their cofactors

Fe^{2+} or Fe^{3+}	Cytochrome oxidase, Catalase, Peroxidase, Xanthine oxidase
Cu^{2+}	Cytochrome oxidase, Lysyl oxidase, Superoxide dismutase
Zn^{2+}	Carbonic anhydrase, Alcohol dehydrogenase, Carboxypeptidase
Mg^{2+}	Hexokinase, Enolase, Glucose-6-phosphatase
Mn^{2+}	Arginase, Enolase, Pyruvate carboxylase
K^+	Pyruvate kinase
Ni^{2+}	Urease
Mo	Dinitrogenase, Xanthine oxidase
Se	Glutathione peroxidase

1.12.1 Naming and classification of enzyme

Many enzymes have common names. For example, trypsin, a proteolytic enzyme, is secreted by the pancreas. Common names provide little information about the reactions that enzymes catalyze. Many enzymes are named for their substrates and for the reactions that they catalyze, with the suffix-*ase* added. As for example, ATPase is an enzyme that helps in breaking down ATP, whereas ATP synthase is an enzyme that helps in synthesis of ATP. Because of the confusion that arose from these common names, an International Commission on enzymes was established to create a systematic basis for enzyme nomenclature.

The enzyme commission has developed a rule for naming enzymes. According to this rule, each enzyme is classified and named according to the type of chemical reaction it catalyzes. The *Enzyme Commission* (EC) has given each enzyme a number with four parts, like EC 2.7.1.2 (Hexokinase). The first three numbers define major *class*, *subclass*, and *sub-subclass*, respectively. The last number is a serial number in the sub-subclass, indicating the order in which each enzyme is added to the list.

Common name and EC numbers of some enzyme

Alcohol dehydrogenase	EC 1.1.1.1
Phosphofructokinase	EC 2.7.1.11
Glutamine synthetase	EC 6.3.1.2
Acetylcholinesterase	EC 3.1.1.7

Systematic classification

The first integer in the EC number designates the class of enzymes. There are six classes to which different enzymes belong. These classes are:

EC 1 Oxidoreductase

Oxidoreductase catalyzes oxidation-reduction reactions.

$A_{red} + B_{ox} \longrightarrow A_{ox} + B_{red}$

Example

Oxidases	Use oxygen as an electron acceptor but do not incorporate it into the substrate.
Dehydrogenases	Use molecules other than oxygen (e.g. NAD^+) as an electron acceptor.
Oxygenases	Directly incorporate oxygen into the substrate.
Peroxidases	Use H_2O_2 as an electron acceptor.

EC 2 Transferases

Transferases catalyze reactions that involve the transfer of groups from one molecule to another. Examples of such groups include amino, carboxyl, carbonyl, methyl, phosphoryl and acyl (RC=O). Common trivial names for the transferases often include the prefix *trans*.

$A{-}B + C \longrightarrow A + B{-}C$

Examples

Transcarboxylases	Transfers a carboxylate group to a substrate.
Transaminases	Transfer amino group from amino acids to keto acids.
Kinases	Transfer phosphate from ATP to a substrate. (ATP → P → substrate)
Phosphorylases	Transfer inorganic phosphate to a substrate. (free P → substrate)

EC 3 Hydrolases

Hydrolases catalyze reactions in which the cleavage of bonds is accomplished by adding water.

$A{-}B + H_2O \longrightarrow A{-}H + B{-}OH$

Example

Phosphodiesterases	Cleave phosphodiester bonds.
Phosphatases	Remove phosphate from a substrate.
Peptidases	Cleave amide bonds such as those in proteins.

EC 4 Lyases

Lyases are enzymes that catalyzes the breaking of C—C, C—O, C—N, C—S and other bonds by means other than hydrolysis or oxidation. These bonds are cleaved by the process of elimination and the result in the formation of a double bond or a new ring, or conversely adding groups to double bonds.

$A = B + HX \longrightarrow A - X + B{-}H$

Example

Aldolases	Removal of aldehydes *via* elimination reactions.
Synthases	Link two molecules without involvement of ATP.
Dehydratases	Removal of H_2O *via* elimination reactions.
Decarboxylases	Removal of CO_2 *via* elimination reactions.

EC 5 Isomerases

Isomerases catalyze several types of intramolecular rearrangements and yield isomeric forms.

$AB \longrightarrow BA$

Example

Mutases	Catalyze the intramolecular transfer of functional groups.
Cis-trans isomerase	Catalyzes the isomerization of geometric isomers.
Epimerases	Catalyze the inversion of asymmetric carbon atoms.
Racemases	Interconvert L and D stereoisomers.

EC 6 Ligases

Join to molecule together at the expanse of an high-energy (phosph bond

Ligases catalyze the formation of C—C, C—S, C—O, and C—N bonds. The energy for these reactions is always supplied by ATP hydrolysis. Other common names for ligases include *synthetases*, because they are used to synthesize new molecules.

A + B + ATP ⟶ A – B + ADP

Example

Carboxylases — Use CO_2 as a substrate.

Biochemical nomenclature distinguishes synthetases from synthases. *Synthases* catalyze condensation reactions in which no nucleoside triphosphate (ATP and GTP) is required as an energy source. *Synthetases* catalyze condensations that *do* use nucleoside triphosphate as a source of energy for the synthetic reaction. A synthase is a lyase and does not require any energy, whereas a synthetase is a ligase and thus requires energy.

1.12.2 What enzyme does?

A chemical reaction between two substances occurs only when an atom, ion, or molecule of one collides with an atom, ion, or molecule of the other. Only a fraction of the total collisions result in a reaction, because usually only a small percentage of the molecules interacting have the minimum amount of kinetic energy that a molecule must possess for it to react. When the reactants collide, they may form an intermediate product whose chemical energy is higher than the combined chemical energy of the reactants. In order for this transition state in the reaction to be achieved, some energy must enter into the reaction other than the chemical energy of the reactants. The transition state is the one with the highest free energy. The difference in free energy between the transition state and the reactants is called the *Gibbs free energy of activation* or simply the *activation energy*.

An enzyme lowers the activation energy of a reaction, thereby increasing the fraction of molecules that have enough energy to attain the transition state and making the reaction go faster in both directions. However, the catalyst does not change the relative energies of the initial and final states. The free energy of reaction, $\Delta G°$, remains unchanged in the presence of a catalyst, so the relative amounts of reactants and products at equilibrium are unchanged. In other words, a catalyst does not influence the position of equilibrium. It only increases the rate of a reaction by lowering the activation energy.

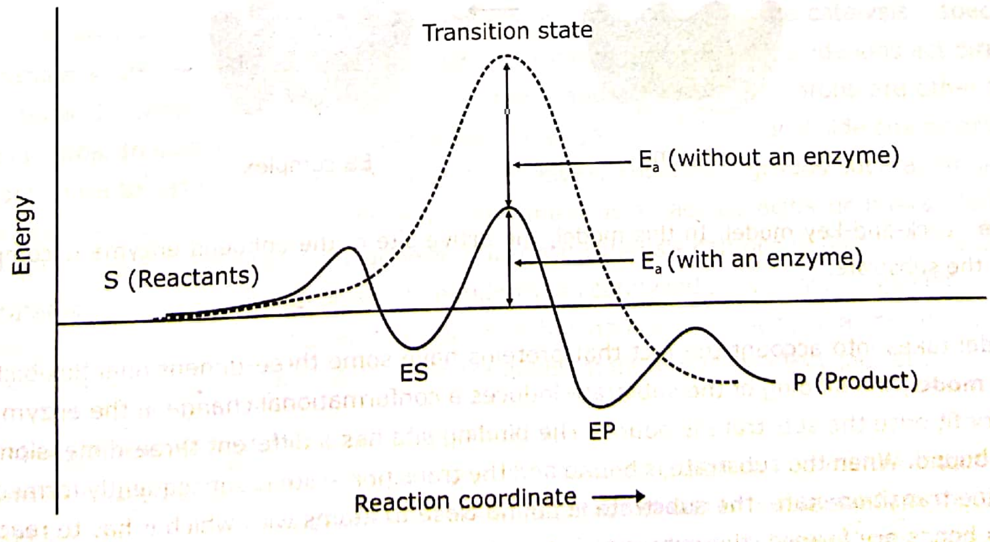

Figure 1.88 Energy profile of a simple enzyme-catalyzed reaction. The non-enzyme catalyzed reaction proceeds via a higher energy transition state and hence the reaction has a higher activation energy than the enzyme catalyzed reaction.