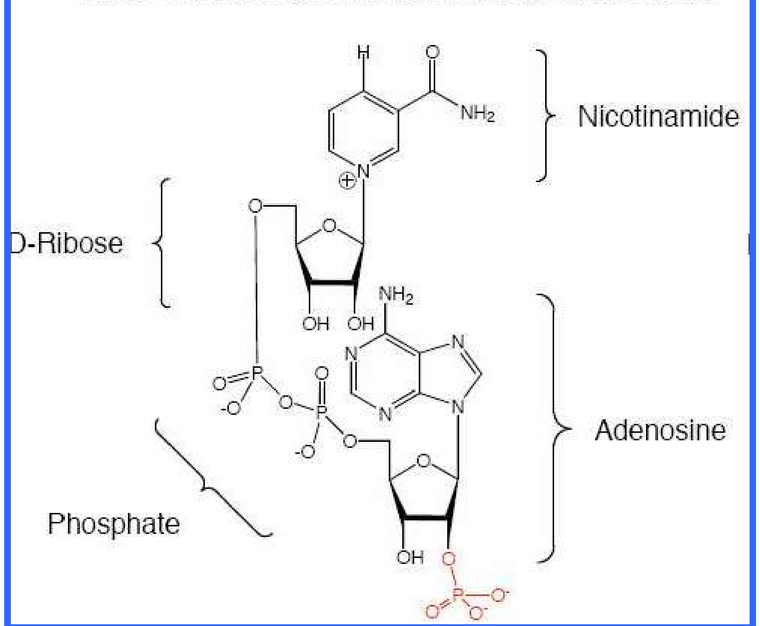
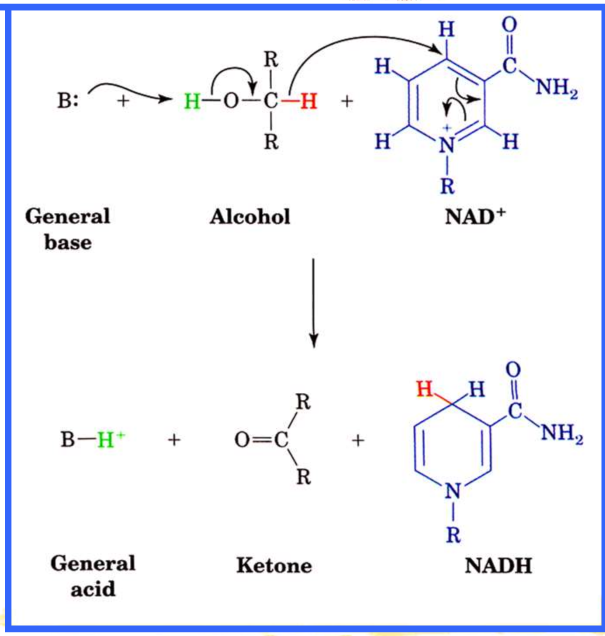
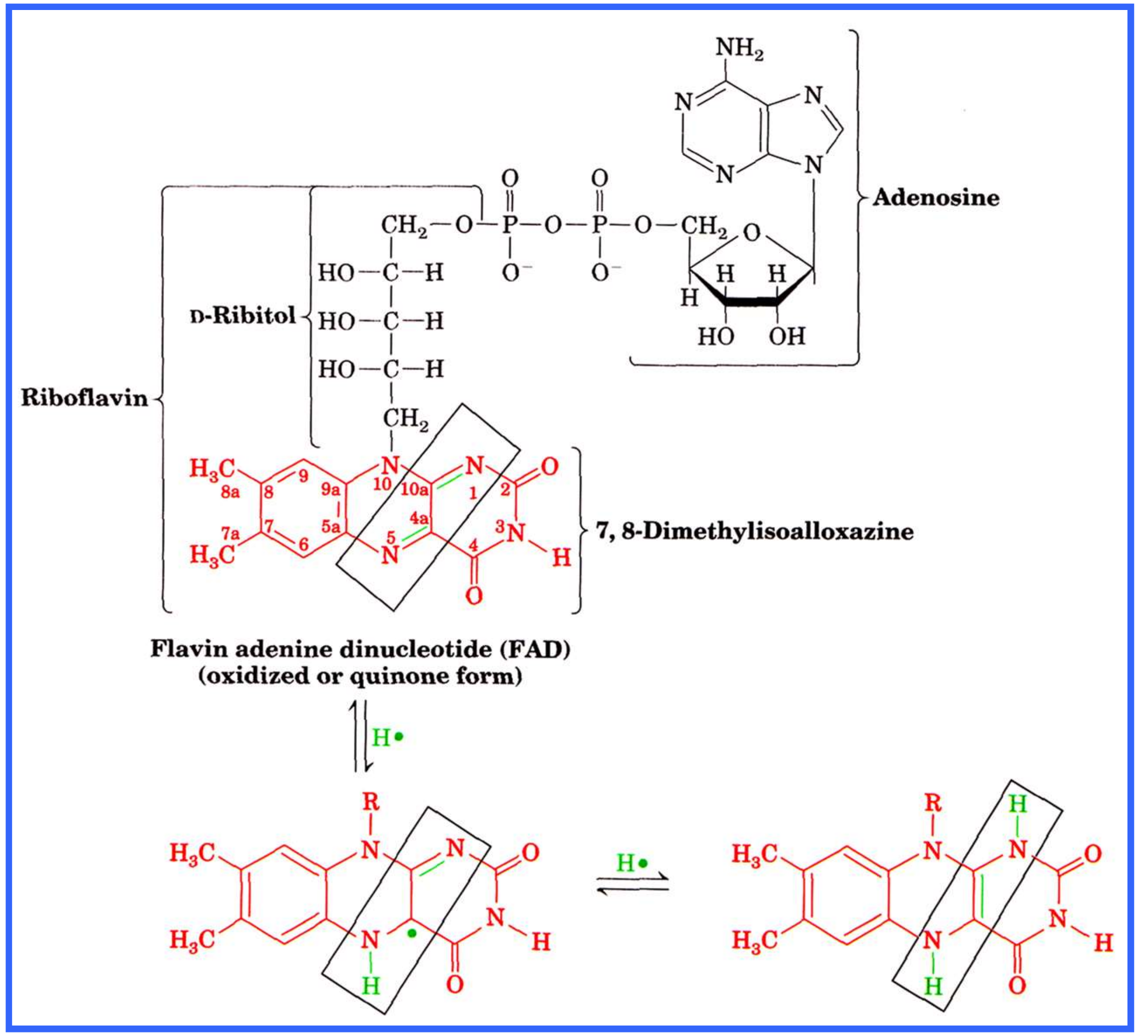
Metabolism: Oxidations and reductions

NAD$^+$: Nicotinamide adenine dinucleotide

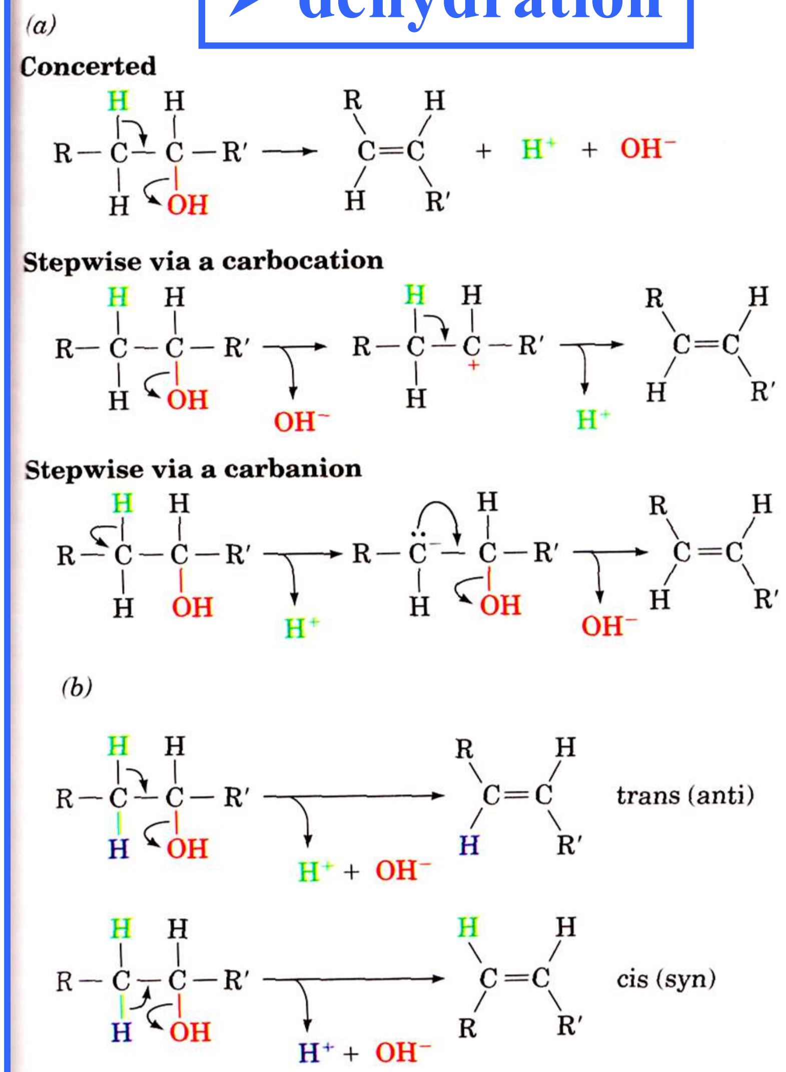




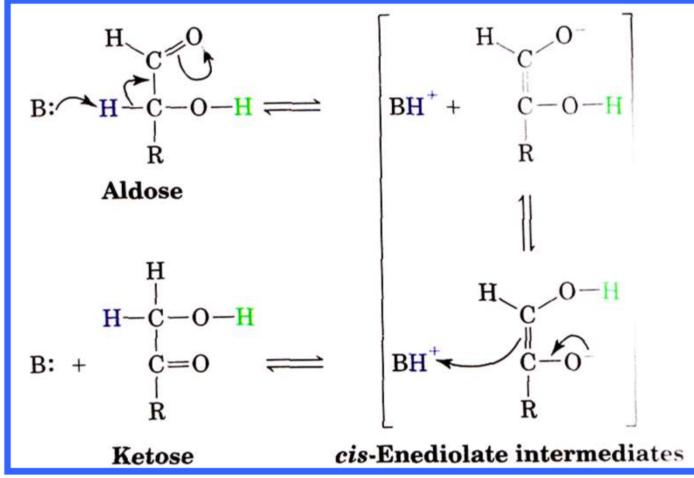


Metabolism: Eliminations, isomerizations, rearrangements

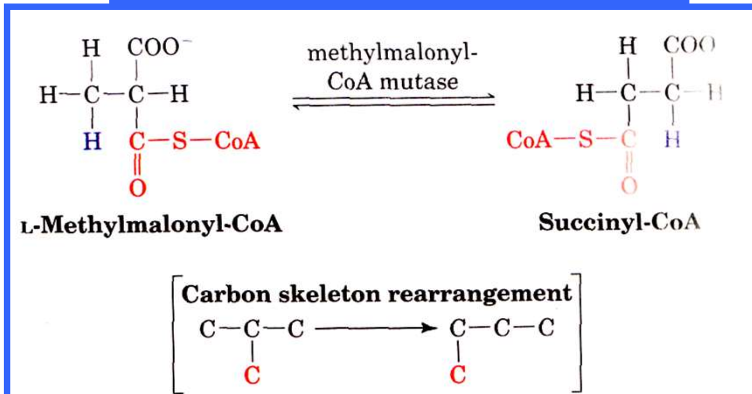
➢ dehydration



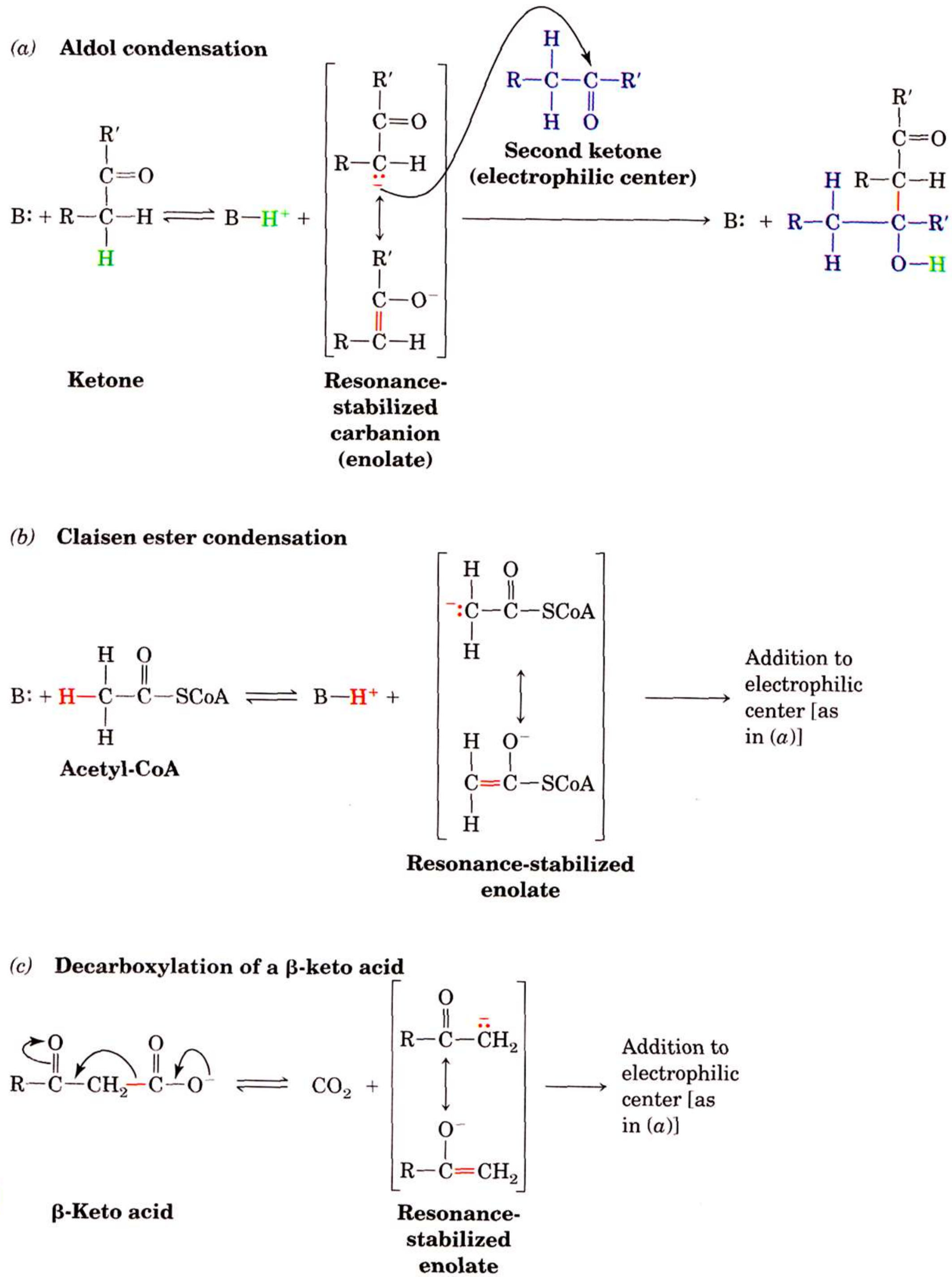
➢ isomerization



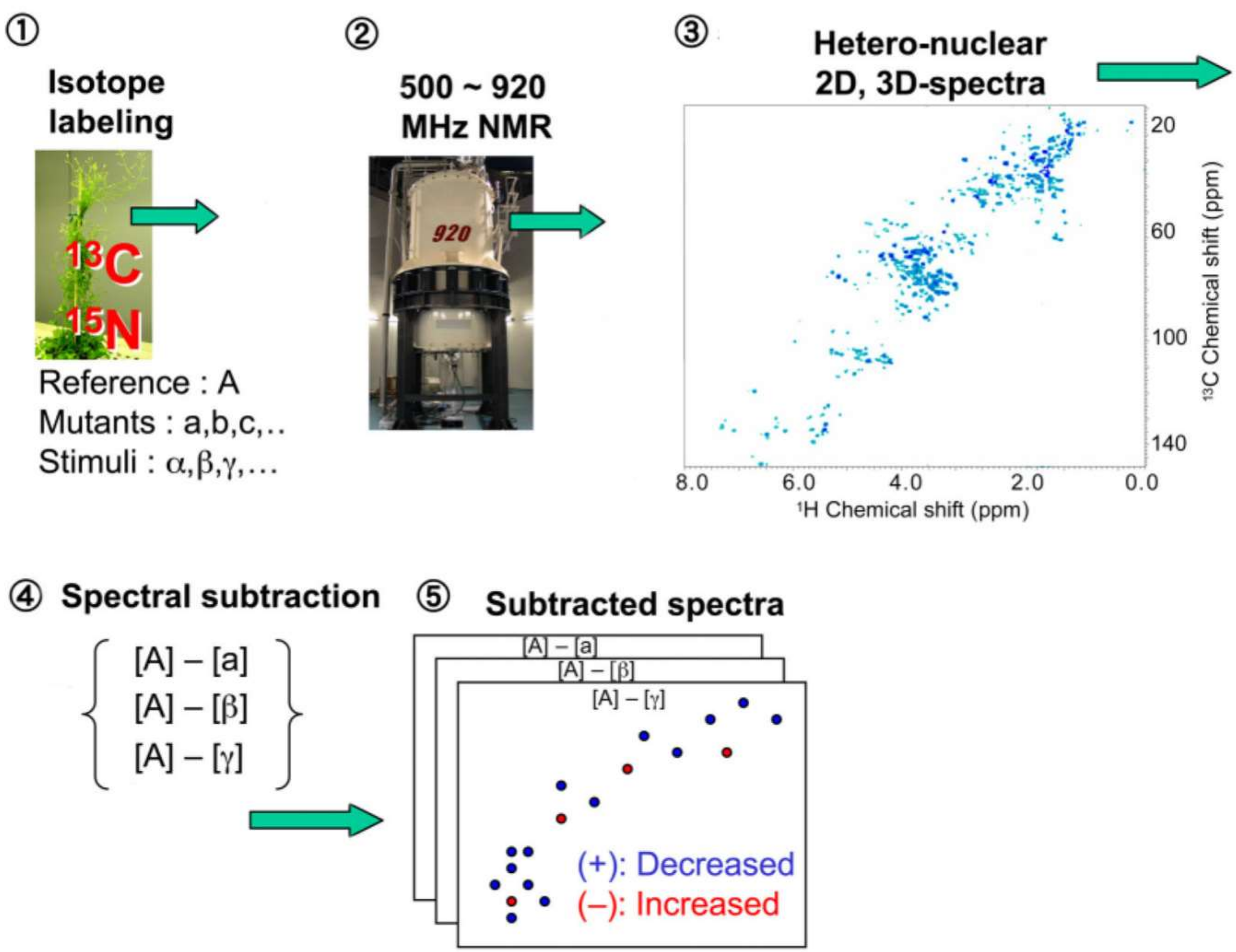
➢ rearrangement



Metabolism: C-C bond formation and cleavage



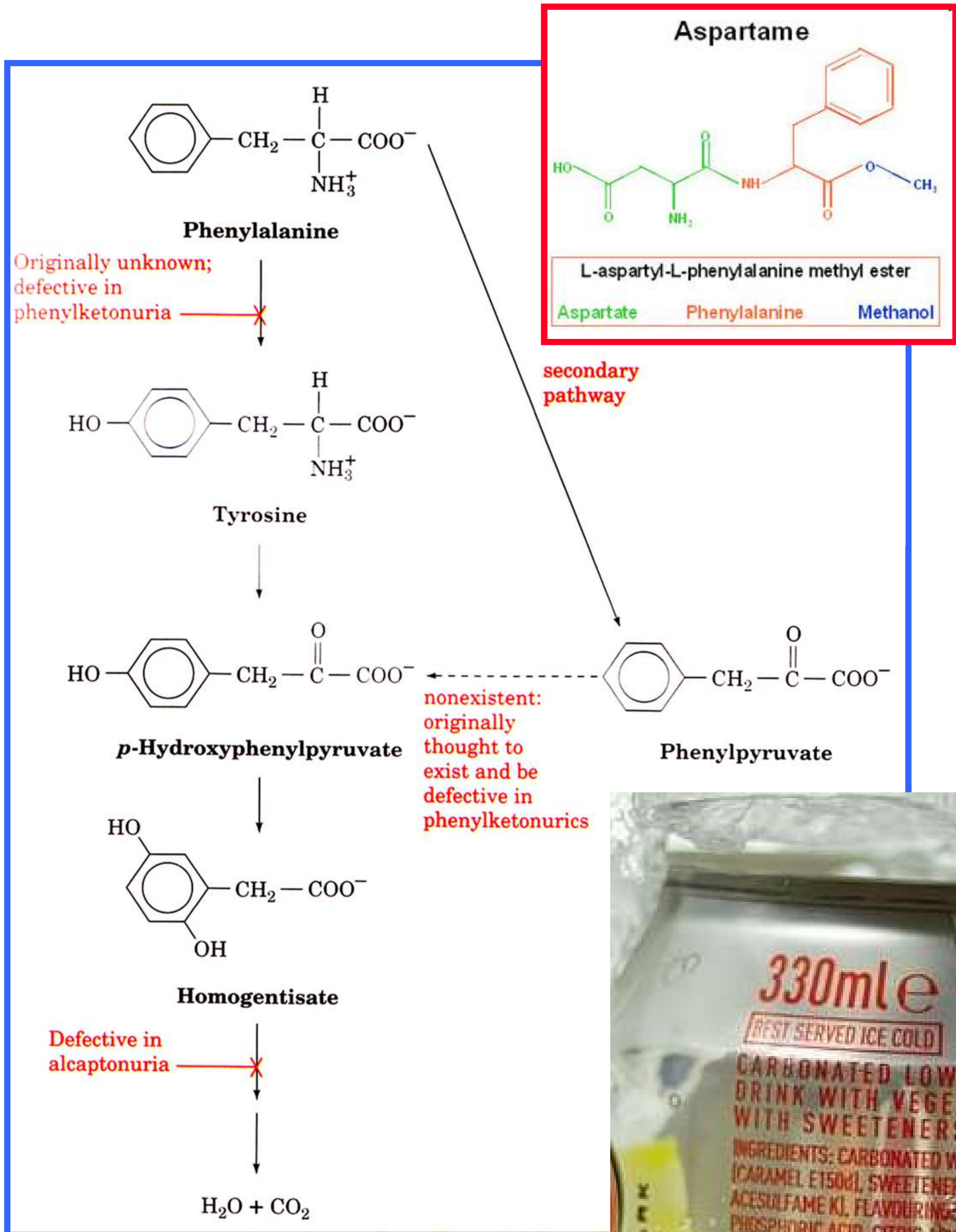
Modern Studies of Metabolism: Metabolomics

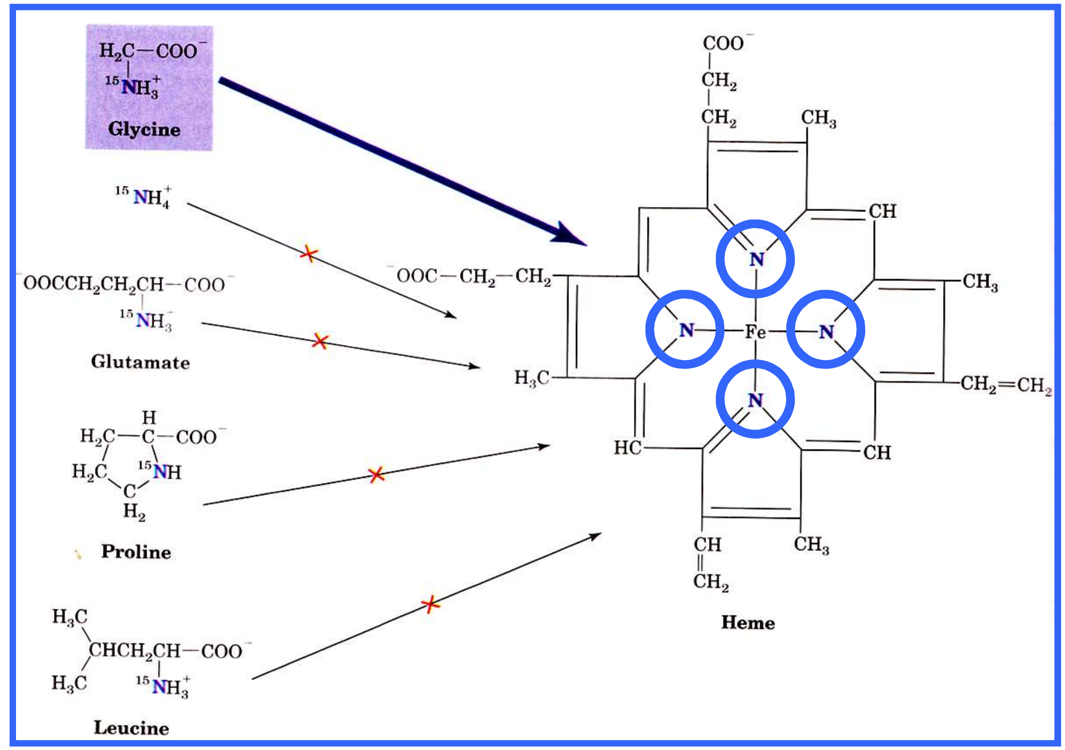


☺ **Pathway intermediates accumulate:**

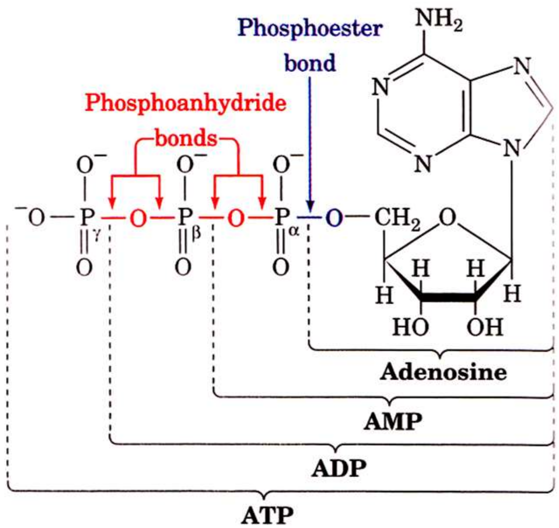
- ➢ **upon genetic manipulation in transgenic animals/plants**
- ➢ **in the presence of metabolic inhibitors**
- ➢ **in the presence of genetic defects**

Phenylketonuria and isotope labeling





ATP: The energizer of the cell



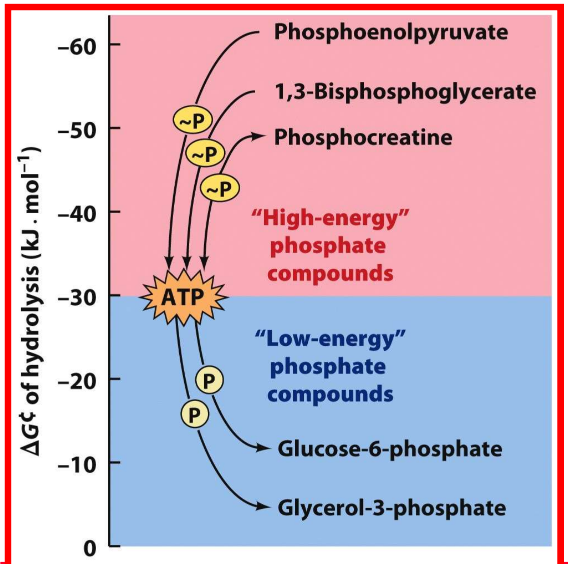
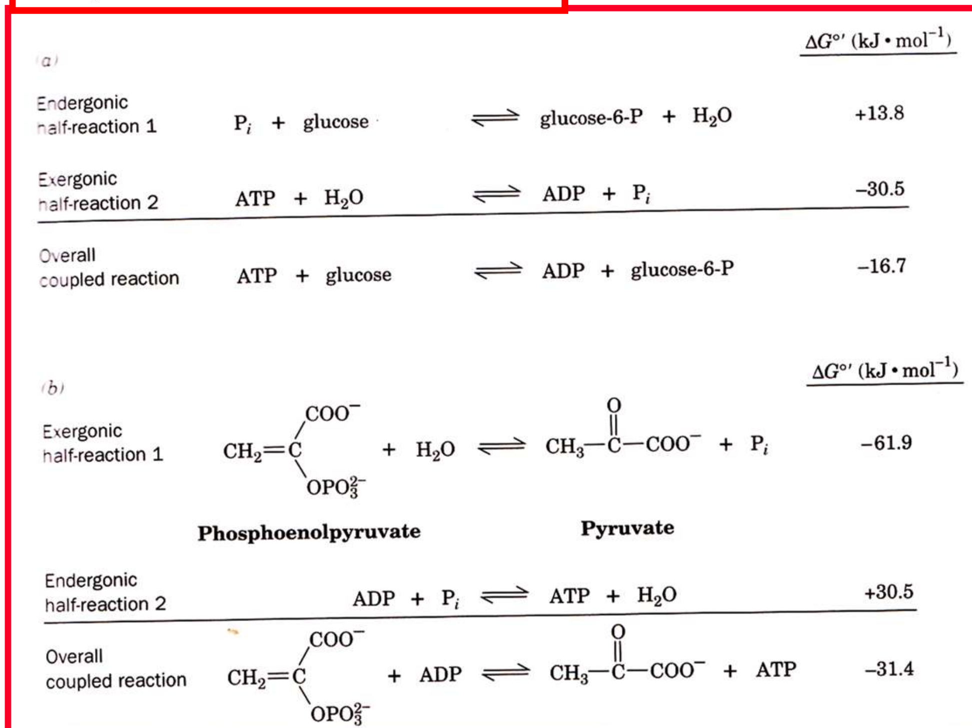


Table 16-3 **Standard Free Energies of Phosphate Hydrolysis of Some Compounds of Biological Interest**

Compound	$\Delta G^{\circ\prime}$ (kJ · mol^{-1})
Phosphoenolpyruvate	−61.9
1,3-Bisphosphoglycerate	−49.4
ATP (→ AMP + PP$_i$)	−45.6
Acetyl phosphate	−43.1
Phosphocreatine	−43.1
ATP (→ ADP + P$_i$)	−30.5
Glucose-1-phosphate	−20.9
PP$_i$	−19.2
Fructose-6-phosphate	−13.8
Glucose-6-phosphate	−13.8
Glycerol-3-phosphate	−9.2

Source: Mostly from Jencks, W.P., *in* Fasman, G.D. (Ed.), *Handbook of Biochemistry and Molecular Biology* (3rd ed.), *Physical and Chemical Data*, Vol. I, *pp.* 296–304, CRC Press (1976).

Table 16-3



Balanced thermodynamics in life

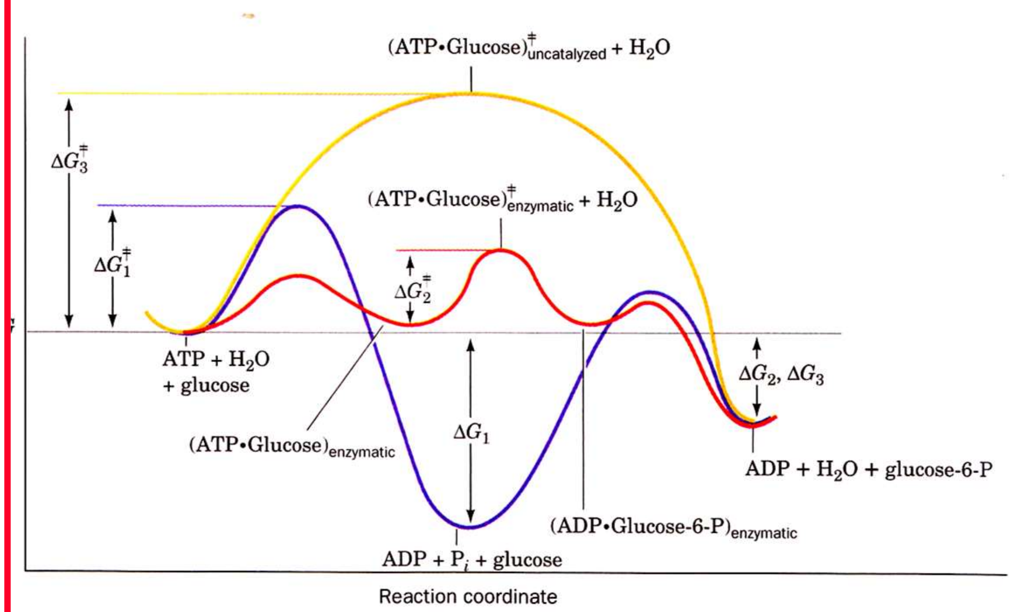
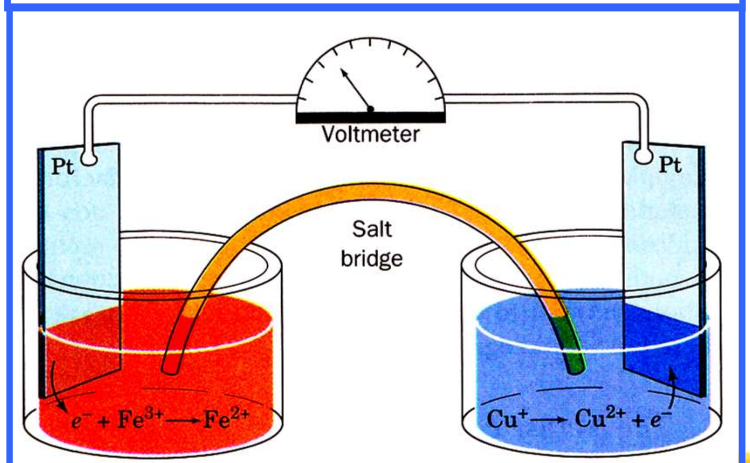


TABLE 16-4 Standard Reduction Potentials of Some Biochemically Important Half-reactions

Half-Reaction	$\mathscr{E}^{\circ\prime}$ (V)
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	0.815
$SO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SO_3^{2-} + H_2O$	0.48
$NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$	0.42
Cytochrome a_3 (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome a_3 (Fe^{2+})	0.385
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.295
Cytochrome a (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome a (Fe^{2+})	0.29
Cytochrome c (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome c (Fe^{2+})	0.235
Cytochrome c_1 (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome c_1 (Fe^{2+})	0.22
Cytochrome b (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome b (Fe^{2+}) (*mitochondrial*)	0.077
Ubiquinone + $2H^+ + 2e^-$ $\rightleftharpoons$ ubiquinol	0.045
Fumarate$^-$ + $2H^+ + 2e^-$ $\rightleftharpoons$ succinate$^-$	0.031
FAD + $2H^+ + 2e^-$ $\rightleftharpoons$ $FADH_2$ (*in flavoproteins*)	−0.040
Oxaloacetate$^-$ + $2H^+ + 2e^-$ $\rightleftharpoons$ malate$^-$	−0.166
Pyruvate$^-$ + $2H^+ + 2e^-$ $\rightleftharpoons$ lactate$^-$	−0.185
Acetaldehyde + $2H^+ + 2e^-$ $\rightleftharpoons$ ethanol	−0.197
FAD + $2H^+ + 2e^-$ $\rightleftharpoons$ $FADH_2$ (*free coenzyme*)	−0.219
$S + 2H^+ + 2e^- \rightleftharpoons H_2S$	−0.23
Lipoic acid + $2H^+ + 2e^-$ $\rightleftharpoons$ dihydrolipoic acid	−0.29
$NAD^+ + H^+ + 2e^- \rightleftharpoons$ NADH	−0.315
$NADP^+ + H^+ + 2e^- \rightleftharpoons$ NADPH	−0.320
Cystine + $2H^+ + 2e^-$ $\rightleftharpoons$ 2 cysteine	−0.340
Acetoacetate$^-$ + $2H^+ + 2e^-$ $\rightleftharpoons$ β-hydroxybutyrate$^-$	−0.346
$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$	−0.421
Acetate$^-$ + $3H^+ + 2e^-$ $\rightleftharpoons$ acetaldehyde + H_2O	−0.581

Source: Mostly from Loach, P.A., *in* Fasman, G.D. (Ed.), *Handbook of Biochemistry and Molecular Biology* (3rd ed.), *Physical and Chemical Data,* Vol. I, *pp.* 123–130, CRC Press (1976).

- **Similarly: Redoxchemistry**



Chapter 16: What have we learned?

☺ **Metabolism: Complex food processing**

☺ **Types of chemistries in metabolism**

☺ **Metabolomics**

☺ **Energy metabolism: ATP and the flow of phosphoryl groups**

☺ **Redox metabolism: NAD^+, FAD and the flow of electrons**