



CHAPTER 9
METABOLISM

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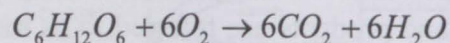
However, when the reactants are present at values close to their equilibrium values, $\frac{[C][D]}{[A][B]} \approx K_{eq}$ and $\Delta G \approx 0$. This is the case for many metabolic reactions, which are said to be **near-equilibrium reactions**. Because their ΔG values are close to zero, they can relatively easily reversed by changing the ration of products to reactants.

When the reactants are in excess of their concentrations, the net reaction proceeds in the forward direction until the excess reactants have been converted to products and equilibrium is attained. Conversely, when products are in excess, the net reaction proceeds in the reverse direction so as to convert products to reactants until the equilibrium concentration ratio is again achieved.

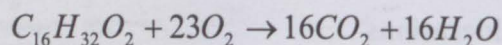
Other metabolic reactions function far from equilibrium; that is, they are irreversible. This is because an enzyme catalyzing such a reaction has insufficient activity to allow it to come to equilibrium. Reactants therefore accumulate in large excess of their equilibrium amounts, making $\Delta G \ll 0$. Changes in substrate concentrations therefore have relatively little effect on the rate of an irreversible reaction; the enzyme is essentially saturated. Only changes in the activity of the enzyme, through allosteric interactions, for example, can significantly alter this rate.

9.2.4 High-energy compounds

The complete oxidation of a metabolic fuel such as glucose:



releases considerable energy ($\Delta G^{\circ'} = - 2850 \text{ kJ}\cdot\text{mol}^{-1}$). The complete oxidation of palmitate, a typical fatty acid,



is even more exergonic ($\Delta G^{\circ'} = - 9781 \text{ kJ}\cdot\text{mol}^{-1}$). Oxidative metabolism proceeds in a stepwise fashion, so the released free energy can be recovered in a manageable form at each exergonic step of the overall process.

9.2.4.1 ATP and Phosphoryl Group Transfer

The “high-energy” intermediate adenosine triphosphate (ATP; **Figure 9.2**), which occurs in all known life forms, is the primary cellular energy currency. ATP consists of an adenosine moiety

(adenine + ribose) to which three phosphoryl ($-PO_3^{2-}$) groups are sequentially linked via a phosphoester bond followed by two phosphoanhydride bonds.

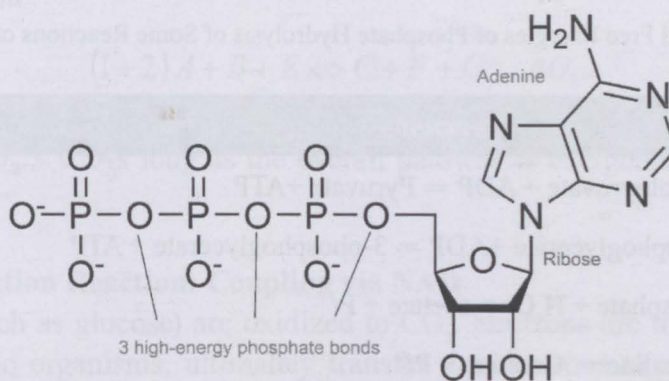
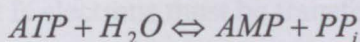
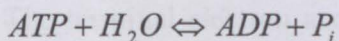


Figure 9.2: The structure of ATP indicating the 3 high-energy phosphate bonds.

The biological importance of ATP rests in the large amount of free energy change that accompanies cleavage of its phosphoanhydride bonds. This occurs when either a phosphoryl group is transferred to another compound, leaving ADP, or a nucleotidyl (AMP) group is transferred, leaving **pyrophosphate** ($-P_2O_7^{4-}$; **PP_i**). When the acceptor is water, the process is known as hydrolysis:



Most biological group-transfer reactions involve acceptors other than water. However, knowing the free energy of hydrolysis of various phosphoryl compounds allows us to calculate the energy of transfer of phosphoryl groups to other acceptors by determining the difference in free energy of hydrolysis of phosphoryl donor and acceptor.

The ΔG° values for hydrolysis of several phosphorylated compounds of biochemical importance are tabulated in **Table 9.1**. The negatives of these values are often referred to as phosphoryl group transfer potentials; they are a measure of the tendency of phosphorylated compounds to transfer their phosphoryl groups to water. Note that ATP has an intermediate phosphoryl-group transfer potential. Under standard conditions, the compounds above ATP in