

Topic: Concept of Free Energy, Redox Potential & Energy Rich Compounds (Part II)

In a chain of consecutive reactions, free energy changes are additive. Like ΔG , standard free energy reaction in different metabolic pathways proceed forward only if the energy change is negative. On examination of the energy changes in the steps of glycolysis it has been found that many of the steps of glycolysis are endergonic ($+\Delta G$), yet the glycolysis pathway reactions proceed forward. Because these reactions are coupled to exergonic reactions; where ATP provides free energy ($-\Delta G$).

Besides, the two ATP-dependent steps, glucose \rightarrow glucose-6-P₁ & Fructose-6-P₁ \rightarrow Fructose 1,6-diP₁

Two other steps, 1,3-bisphosphoglycerate \rightarrow 3 Phosphoglycerate & Phosphoenol Pyruvate \rightarrow Enolpyruvate are highly exergonic. The standard free energy generated are ΔG° are -49 kJ/mol and -61.9 kJ/mol .

Thus, these two energy changes are sufficient for synthesis of two ATP and also to drive the pathway forward irrespective of other endergonic reactions.

Besides considering standard free energy change in terms of concentrations of reactants and products, one can consider ΔG in simpler way, that is, in terms of difference in free energy content of reactants and products. If the free energy content of products is more than that of reactants, the reaction is exergonic ($-\Delta G$) under standard conditions and hence is spontaneous.

Contrary to above, if the free energy content of reactant is less than that of products, the reaction will proceed in reverse direction. To move the reaction in forward direction, external source of free energy will be required for the reactant.

Redox Potential: - It is a measure

of a chemical reaction species to acquire electrons from or lose electrons to an electrode and thereby be reduced or oxidised respectively. Redox Potential is usually measured

13
in volts (V) or millivolts (mV). Each species has its own intrinsic redox potential. For example, the more positive the reduction potential, the greater the species affinity for electrons and tendency to be reduced. ORP can reflect the antimicrobial potential of the water.

Similar to how the concentration of hydrogen ion determines the acidity or pH of an aqueous solution, the tendency of electron transfer between a chemical species and an electrode determines the redox potential of an electrode couple. Like pH, redox potential represents how easily electrons are transferred to or from species in solution. Redox potential characterises the ability under the specific conditions of a chemical species to lose or gain electrons instead of the amount of electrons available for oxidation or reduction.

In fact, it is possible to define pH, the negative logarithm of

Electron Concentration i.e. $(- \log [e^-])$ in a solution, which will be directly proportional to the redox potential. Sometimes pe is used as a unit of reduction potential instead of E_h ; for example, in Environmental chemistry; if we normalize pe of hydrogen to zero, we will have the relation $pe = 16.9 E_h$ at room temp. This point of view is useful for understanding redox potential, although the transfer of electrons, rather than the absolute concentration of free electrons, is the central equilibrium, is how one usually thinks of redox potential. Concept of Half Cell is also based on this redox potential difference of a system.

Energy Rich Compounds

As we all know Sun is the ultimate and primary source of free energy for synthesis of ATP and carbohydrates in plants. Both Exergonic and Endergonic reactions are involved in photosynthesis. Animals utilize plants and their products as nutrients, which are degraded enzymatically to small molecular forms suitable for intestinal absorption and

assimilation. The assimilated molecules are utilized for synthesis of high-energy compounds, biopolymers, vitamins and hormones.

The high energy phosphates such as ATP, Guanosine triphosphate (GTP), Uridine triphosphate (UTP), Cytidine triphosphate (CTP) and Thymidine triphosphate (TTP), are utilised for synthesis of nucleic acids, proteins, polyelectrolytes and so on.

Energy comes through exergonic process from high-energy phosphates and is utilized for synthetic processes through endergonic process.

It was Lipmann who introduced the expression of $\sim(P)$ for high-energy bonds in high-energy phosphates. High Energy Phosphate molecules possess different values for ΔG° after their hydrolysis.

ATP as High Energy molecule and its role in Energy transfer.

Most Common Energy rich Compound is ATP. It possesses three phosphate groups. The three phosphates (α, β and γ) are linked to each other linearly by oxygen bonds.

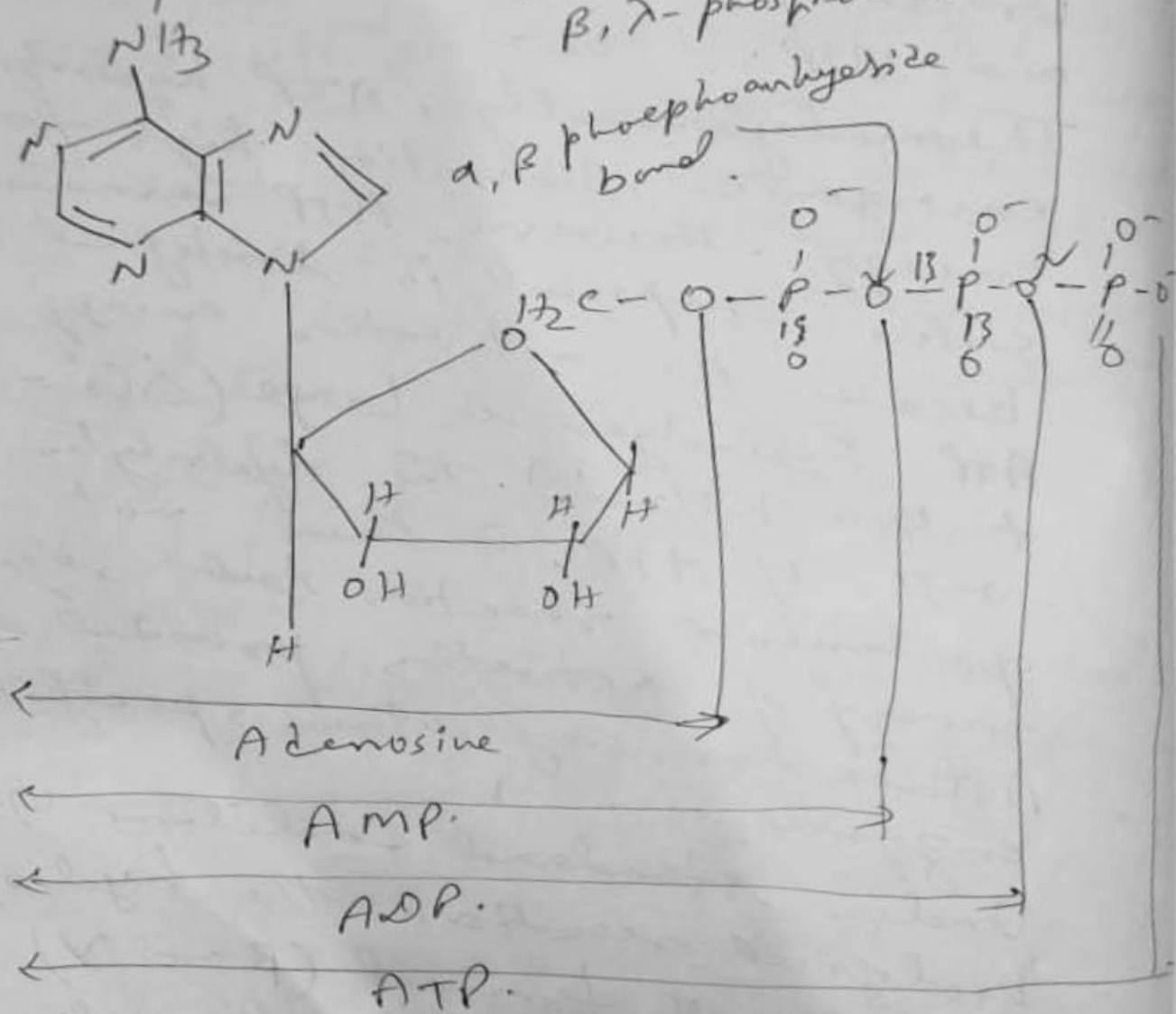
The phosphoanhydride bonds linking α , β and λ phosphates are named as α , β phosphoanhydride and β , λ - phosphoanhydride bonds. In Cellular systems, both ATP and ADP are bound to Mg^{2+} in forming $MgATP^{2+}$ and $MgADP$ complex. Replacing Adenine by Guanine provides structures of GTP and GDP (Guanosine diphosphate). Likewise, replacing purine base by pyrimidine base, Cytosine or Uracil provides CDP (Cytidine diphosphate) or CTP and Uracil provides UDP (Uridine diphosphate) and UTP.

Thermodynamically, ATP hydrolysis is exergonic, liberating high free energy. However, ATP remains a stable compound in biological systems because the activation energy for ATP hydrolysis is large ($\Delta G^\circ = +200$ to 400 KJ/mol). The hydrolytic cleavage of ATP, is thus not a spontaneous reaction but requires energy of activation provided by ATPase or any other specific enzymes.

Under standard conditions of biological reactions, the hydrolytic cleavage of terminal (β and γ) phosphoanhydride bond releases

[19]

ΔG° of -30.5 kJ/mol of energy. The inorganic phosphate, removal possesses four oxygens, two of which are $-$ vely charged. one possesses a proton and the fourth is linked to phosphorus by a double bond. However, the protons spin around the phosphorus through oxygen and imparts double bondal nature to all P-O bonds. These two forms of inorganic PO_4 forms a hydrid pair



Structure of AMP, ADP and ATP

[Pg-8]

Ionization of ADP releases its terminal proton imparting another negative charge to the other oxygen. Further, hydrolysis of ADP removes the second inorganic P_{O_4} with the release of ΔG° of -27.6 kJ/mol . Hydrolysis of phosphoanhydride bond produces ATP and P_i with the release of ΔG° of -45.6 kJ/mol . However, as the actual conditions of reactants, products, pH, temperature and so on are different in a particular cellular system, the ΔG° of ATP hydrolysis will be different.
